REACTIONS OF CESIUM ALLOYS WITH AROMATIC HYDROCARBONS AND ALKYL CHLORIDES

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REACTIONS OF CESIUM ALLOYS WITH AROMATIC HYDROCARBONS AND ALKYL CHLORIDES

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SUMMARY

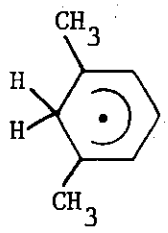
The purpose of this research was to investigate the reactions of cesium-potassium alloy and cesium-potassium-sodium alloy with aromatic hydrocarbons and alkyl chlorides. The compounds investigated were benzene, toluene, t-butylbenzene, m-xylene, p-xylene, biphenyl, diphenylmethane, 2,2-diphenylpropane, 1,1,1-triphenylethane, bibenzyl, 1,2-di-p-tolyethane, 2,3-dimethyl-2,3-diphenylbutane, 1,2,2-triphenylpropane, 1,3-diphenylpropane, cyclohexyl chloride, and 2,2,3-triphenylpropyl chloride.

Reaction of benzene with excess Cs-K-Na alloy at -45°C in THF produces cesium benzenide (I) as a black solid. After three hours at -45°C, dicesium 1,1-'dihydrobiphenylide (II), a yellow solid, is formed by the intramolecular coupling of I. Compound II upon protonation with water gave a 75.7 mole % yield of 1,1',4,4'-tetrahydrobiphenyl (III) whose structure was ascertained by ^{1}H NMR, ^{13}C NMR, and mixture gc injections with an authentic sample of III.

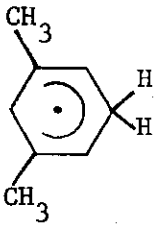
Reaction of toluene with excess Cs-K-Na alloy at -45° in THF produces initially cesium toluenide (IV) as a black solid. After three hours at -45°C, dicesium 3,3'-dimethyl-1,1'-dihydrobiphenylide (V), a yellow solid is formed by the intermolecular coupling of IV. Compound V upon protonation with water gave a 56.3 mole % yield of 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl (VI) whose structure was ascertained by ^{1}H NMR, ^{13}C NMR, UV, IR, MS, elemental analysis, and dehydrogenation. Dehydrogenation of

the dimeric products with excess DDQ gave 3,3'-dimethylbiphenyl (99.1%), 2,3'-dimethylbiphenyl (0.7%), and 2,2-dimethylbiphenyl (0.2%). Thus the dimerization of IV favors coupling of the radical anion at the position meta to the methyl group by 99.5%.

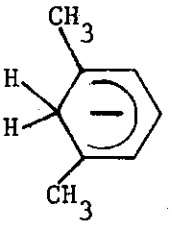
Reaction of m-Xylene with excess Cs-K-Na alloy at -48°C in THF produces initially cesium m-xylenide (VII) as a black solid. After three hours at -45°C, dicesium 3,3',5,5'-tetramethyl-1,1'-dihydrobiphenylide (VIII), a yellow solid, is formed by the intermolecular coupling of VII. Compound VIII upon protonation with water gave a 54.8 mole% yield of 3,3',5,5'-tetramethyl-1,1',4,4'-tetrahydrobiphenyl (IX) whose structure was ascertained by ^{1}H NMR, ^{13}C NMR, UV, IR, MS, elemental analysis, and dehydrogenation. In the presence of 18-crown-6 VII is quantitatively protonated to apparently form radicals X and XI, which are rapidly reduced by the alloy to anions XII and XIII respectively. Deuteration and carbonation of anions XII and XIII indicate that these



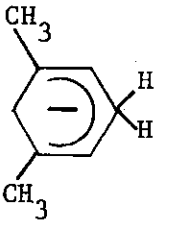
X



XI



XII



XIII

anions and their radical precursors are in a 3.8 : 1.0 ratio.

Both p-xylene and t-butylbenzene fail to react with Cs-K-Na alloy at -45°C in THF.

Reactions of bibenzyl with Cs-K-Na alloy at -75°C likely produces dicesium 1,2-diphenylethanide which rapidly cleaves to benzylcesium, the

latter after carbonation gives phenylacetic acid in nearly quantitative yield. Under these reaction conditions, the radical anions of 2,3-dimethyl-2,3-diphenylbutane and 1,2,2-triphenylpropane but not 1,2-di-p-tolylethane are quantitatively cleaved to give the appropriate benzyl anions.

Analysis of the cesium alloy for the reacting alkali metal in reaction of Cs-K alloy with benzene, 1,3-diphenylpropane, and 2,2-diphenylpropane at -20°C in THF or the reaction of Cs-K-Na alloy with benzene, toluene, 1,3-diphenylpropane, 1,2,1-triphenylethane, and 1,2,2-triphenylpropyl chloride at -45°C in THF shows that cesium metal is selectively removed from the alloy during reaction. Since both metals in Cs-K alloy can react with biphenyl or cyclohexyl chloride at 25°C in THF, analysis of the alloy under these conditions indicated that the ratio of cesium to potassium removed from the alloy was 10 : 1, a result which demonstrates the superior reducing ability of cesium metal in THF.

CHAPTER I

INTRODUCTION

The purpose of this research was to investigate the reactions of cesium and potassium alloy[1] and/or cesium, potassium, and sodium alloy[2] with aromatic hydrocarbons and alkyl chlorides. The compounds investigated were benzene, toluene, t-butylbenzene, m-xylene, p-xylene, biphenyl, diphenylmethane, 2,2-diphenylpropane, 1,1,1-triphenylethane, bibenzyl, 1,2-di-p-tolylethane, 2,3-dimethyl-2,3-diphenylbutane, 1,2,2-triphenylpropane, 1,3-diphenylpropane, cyclohexyl chloride, and 2,2,3-triphenylpropyl chloride. The reaction of aromatic hydrocarbons with alkali metals to form radical anions and dianions has been recently reviewed.[3,4,5]

Grovenstein and coworkers[6] discovered that molten cesium metal in THF at 40°C reacts with 4-chloro-1,1,1-triphenylbutane to give the novel

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[1] M. Hansen, "Constitution of Binary Alloys." McGraw-Hill, New York, 1958, p. 576. The minimum melting alloy composition is 50 atom % Cs and 50 atom % K, mp -37.5°C.

[2] F. Teppler, J. King, and J. Greer, The Alkali Metals, An International Symposium, Held at Nottingham on 19-22nd July, 1966. The Chemical Society, London, 1967, p. 25. The minimum melting alloy composition is 40.8 atom % Cs, 47.4 atom % K, and 11.8 atom % Na, mp -79.2°C.

[3] N. L. Holy, Chem. Rev., 74, 243 (1974).

[4] T. H. Longfield, Ph.D. Thesis, "Reactions of Cesium with Aromatic Hydrocarbons." Georgia Institute of Technology, 1973, p. 1.

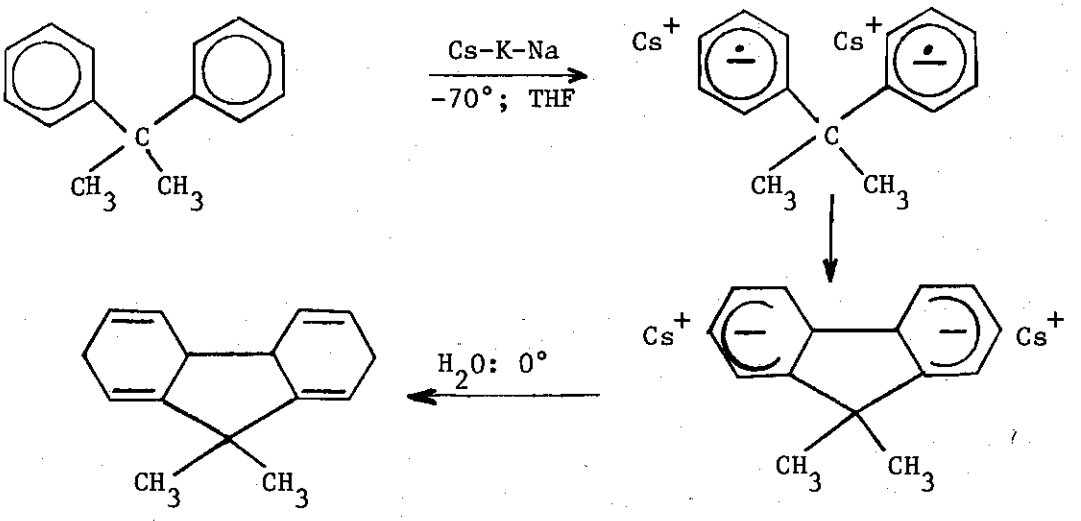
[5] E. S. Petrov, M. I. Terekhova, and A. I. Shatenshtein, Russ. Chem. Rev., 42, 713 (1973).

[6] E. Grovenstein, Jr., J. A. Beres, Y-M. Cheng, and J. M. Pegolotti, J. Org. Chem., 37, 1281 (1972).

product 9-phenyl-9-n-propylfluorene. Since similar reactions of the chloride with two equivalents of cesium-potassium alloy at -45°C gave considerable 1,1,1-triphenylbutane, the reactive carbanion must be protonated during the reaction. Thus the precursor of the 9-phenyl-9-n-propyfluorene may be 1,1,1-triphenylbutane which then reacts with additional cesium metal to form a diradical anion which couples to form the fluorene system. This mechanism was confirmed by the reaction of 1,1,1-triphenylethane with an excess of Cs-K-Na alloy at -70°C in THF to give a red intermediate, which upon protonation, gave an almost quantitative yield of 9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene. An analogous reaction was found to occur with 1,1,1-triphenylbutane.

Longfield[7] found that 2,2-diphenylpropane reacts with an excess of Cs-K-Na alloy at -70°C in THF to give a red intermediate, which upon protonation gave an almost quantitative yield of cis-9,9-dimethyl-2,4a,

Scheme 1

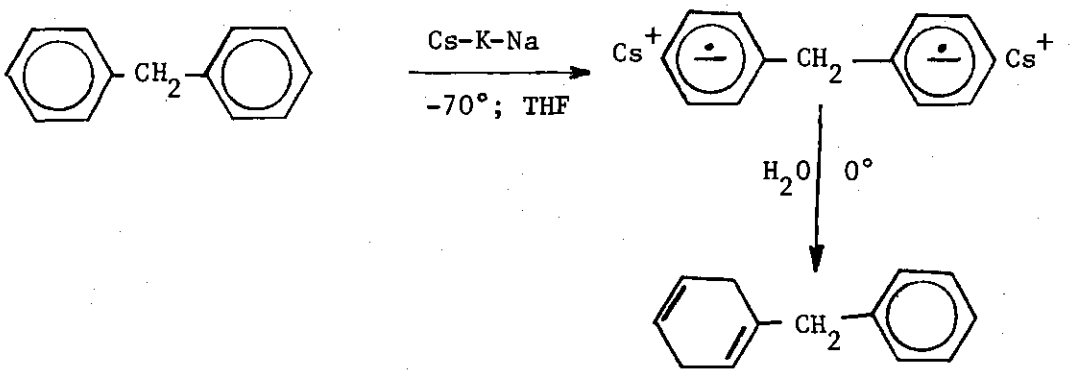


[7]Reference 4, p. 123.

4b,7-tetrahydrofluorene (see Scheme 1). The cis-9,9-dimethyl-2,4a,4b,7-tetrahydrofluorene was identified by UV, ^{1}H NMR, mass spectra, elemental analysis, and dehydrogenation to 9,9-dimethylfluorene. Young and Bauld[8] have shown through an ESR study that 2,2-diphenylpropane radical anion cyclizes to 9,9-dimethylfluorene radical anion.

The reaction of diphenylmethane[9] with excess Cs-K-Na alloy in THF at -70°C gives a black precipitate, which upon protonation gives 2,5-dihydrodiphenylmethane. The black precipitate has a broad-line ESR spectrum indicative of a high yield of radical anion in the doublet state. It is likely that the reaction proceeds as outlined in Scheme 2.

Scheme 2



Dehydrogenation of this reaction mixture with Pd/C gave diphenylmethane and no fluorene. An attempt to facilitate cyclization by warning of the reaction mixture to -60°C resulted in the formation of the diphenylmethyl anion (Scheme 3). Hackspill[10] reports that both diphenylmethane and

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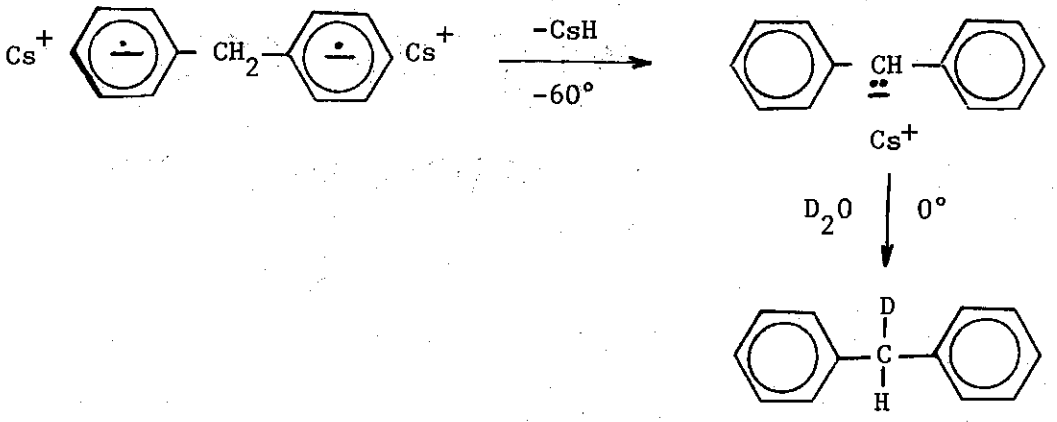
[8] J. D. Young and N. L. Bauld, Tetrahedron Lett., 25, 2251 (1974).

[9] Reference 4, page 132.

[10] L. Hackspill, "Nouveau Traitè de Chemie Minerale." Vol. 3, P. Pascal, Ed., Masson, Paris, 1956, p. 124.

Scheme 3



triphenylmethane react with cesium metal to give diphenylmethylcesium and triphenylmethylcesium respectively. The diphenylmethylcesium gave diphenylacetic acid on carbonation. In similar work Gilman and Young[11] have shown that triphenylmethane reacts with sodium-potassium alloy in ether to give a red compound which upon carbonation gives triphenylacetic acid. This red compound was identified as triphenylmethylpotassium by precipitation and flame tests for potassium. House and Kramer[12] have found that the reaction of triphenylmethane with potassium in DME produce solutions of triphenylmethylpotassium containing various cleavage and reduction products derived from triphenylmethane. Thus after hydrolysis diphenylmethane, biphenyl, reduced biphenyls, and triphenylmethane were isolated from the reaction. Theilacker and Moellhoff[13] have found that potassium (and not sodium) in ether will cleave tripticene to

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[11] H. Gilman and R. V. Young, J. Org. Chem., 1, 315 (1936).

[12] H. O. House and V. Kramer, J. Org. Chem., 27, 4146 (1962).

[13] W. Theilacker and E. Moellhoff, Angew. Chem., 74, 781 (1962).

give after protonation by methanol 9-phenyl-9,10-dihydroanthracene. They have also found that triphenylmethane and tetraphenylmethane are cleaved by potassium in ether to give after carbonation diphenylacetic acid and triphenylacetic acid. Longfield[14] found that the reaction of tetraphenylmethane with Cs-K-Na alloy in THF at -70°C gave after hydrolysis biphenyl, diphenylmethane, tetraphenylmethane, and reduction products of biphenyl, triphenylmethane, 9-phenylfluorene, and tetraphenylmethane. The ESR spectrum of the radical anion of triphenylmethane in DME disappears at temperatures above -60°C and the triphenylmethyl carbanion and the radical anion of biphenyl are formed.[15] ESR studies of the radical anions of diphenylmethane,[16,17] 1,2-diphenylethane (bibenzyl),[16,17] 1,2-di-*p*-tolylethane,[17] 2,2-diphenylpropane,[17] 1,3-diphenylpropane,[16,17] and 1,5-diphenylpentane[17] indicate that the unpaired electron is localized on only one phenyl ring and that these compounds all exhibit a five line ESR[17] spectrum similar to that of toluene. At -70°C in THF-DME, the radical anion of diphenylmethane decomposes to give the spectrum of the biphenyl radical anion.[16] The presence of secondary paramagnetic products indicate that further chemical reactions have taken place. Decomposition of the final products of the reaction of diphenylmethane with potassium with carbon dioxide or oxygen gave diphenylacetic acid (80%) or

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[14] Reference 4, p. 206.

[15] R. N. Nasirov, A. I. Prokof'ev, S. P. Solodovnikov, and M. I. Kabachnik, Izv. AN SSSR, ser. khim. 9, 1981 (1973).

[16] V. M. Kazakova, B. I. Shapiro, G. Makarov, and Ya. K. Syrkin, Dokl. Akad. Nauk SSSR, 165, 1340 (1965).

[17] I. I. Grandberg, V. B. Golubev, and O. R. Khrolova, Zh. Strukt. Kim., 8, 1021 (1967).

tetraphenylethane (80%) respectively.[17] The ESR spectrum of stilbene indicates that the radical anion is delocalized over the entire molecule.[18] It is expected that an electron could move freely from ring to ring, since the π-systems of the aromatic rings are in conjugation through the π-system of the bridging double bond.

Hackspill[19] in 1912 reported that benzene reacts with cesium at 28°C to give a black solid containing cesium in an amount near that expected for phenylcesium. He suggested that the substance was phenylcesium although it was formed without evolution of hydrogen and gave biphenyl and hydrogen on hydrolysis. Hackspill[20] later questioned this structure and noted that the product merited further study. Subsequently de Postis[21] came to the conclusion that the black compound had the formula $C_6H_6Cs_6$. Clusius and Mollet[22] found that cesium reacts with benzene at 50-60°C with the steady evolution of hydrogen and that the black product reacts with water to give biphenyl and phenol.

Longfield[23] found that the reaction of excess benzene with finely divided cesium in THF at -70°C gives a black precipitate which has a broad line ESR spectrum indicative of a high yield of radical anion in the

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[18] V. V. Voevodskii, S. P. Solodovnikov, and V. M. Chibrikin, Dokl. Akad. Nauk SSSR, 129, 1082 (1959).

[19] L. Hackspill, Proc. Int. Congr. Appl. Chem., 8th, 2, 113 (1912); Ann. Chim. Phys. (Paris), 28, 653 (1913).

[20] L. Hackspill, Helv. Chim. Acta, 11, 1026 (1928).

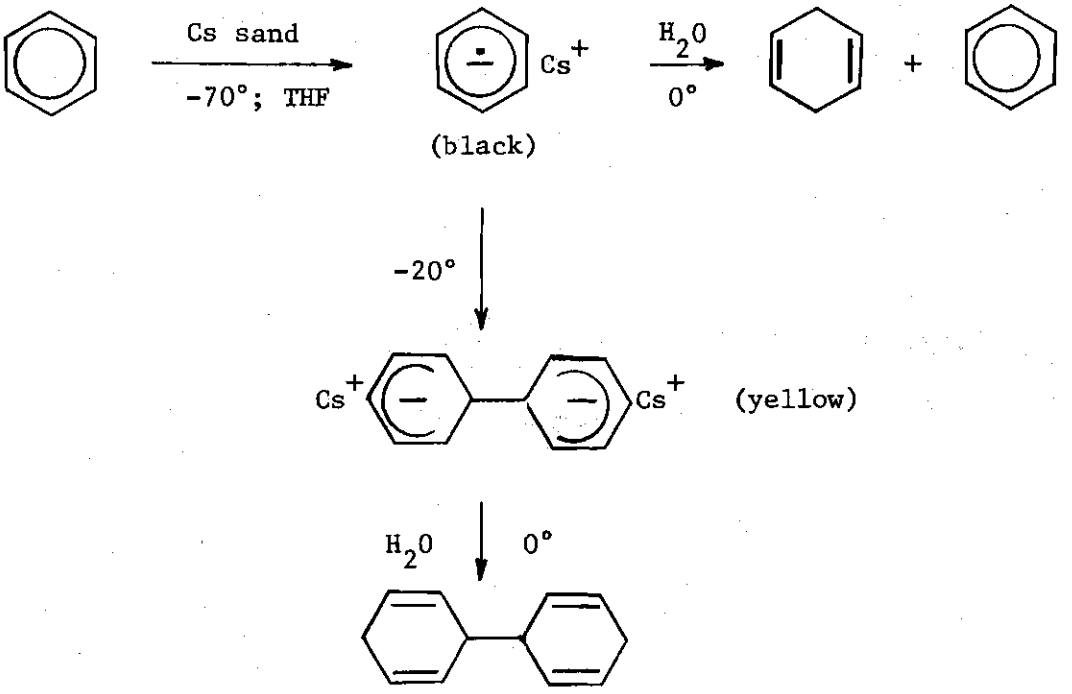
[21] J. de Postis, Proc. Intl. Cong. Pure Appl. Chem., 11th, 5, 867 (1947).

[22] K. Clusius and H. Mollet, Helv. Chim. Acta, 39, 370 (1956).

[23] Reference 4, p. 62.

doublet state. Protonation of this reaction mixture after 1.5 hours gave the products (in yields expressed as percent of starting cesium converted into product) 1,4-dihydrobenzene (70%), cyclohexene (3%), and 1,1',4,4'-tetrahydrobiphenyl (6%). With an increase of temperature to

Scheme 4



-20°C the black precipitate is converted into a yellow diamagnetic precipitate; protonation gave 1,4-dihydrobenzene (36%) and 1,1',4,4'-tetrahydrobiphenyl (39%). The 1,1',4,4'-tetrahydrobiphenyl was identified by UV, IR, ^{1}H NMR, mass spectra, elemental analysis, and dehydrogenation to biphenyl. Warming of the yellow precipitate to 35°C gives a black precipitate which is dicesium biphenylide according to its reaction with iodine to give biphenyl or with water which gives a mixture of hydrocarbons

like that from dicesium biphenylide[24] prepared by the reaction of biphenyl with excess cesium in THF. Dicesium biphenylide has the same emperical composition as phenylcesium; evidently, the compound prepared by Hackspill[19] was largely dicesium biphenylide.

In related work Beguin and Setton[25] found that benzene reacts with a potassium-graphite lamellar compound (KC_8) in THF at 20°C to give a blue compound in an unspecified yield. Hydrolysis of this compound gave mainly biphenyl and also reduction products which evidently are identical to those obtained by Longfield from the reaction of benzene or biphenyl with cesium at 35°C (see Scheme 5).

Spin concentration measurements by ESR indicate that potassium does not extensively react with benzene in THF-DME, since at temperatures between -83°C and 18°C the radical anion yield did not exceed 0.09%.[26,27] This is quite low when compared to a radical anion yield obtained by Longfield[28] from the reaction of cesium with benzene in THF at -75°C. It has been shown by a study[29] of the equilibrium constants that the radical anions of alkyl substituted benzenes are less likely to form than

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[24]Reference 4, p. 111.

[25]Beguin and R. Setton, Chem. Commun., 611 (1976).

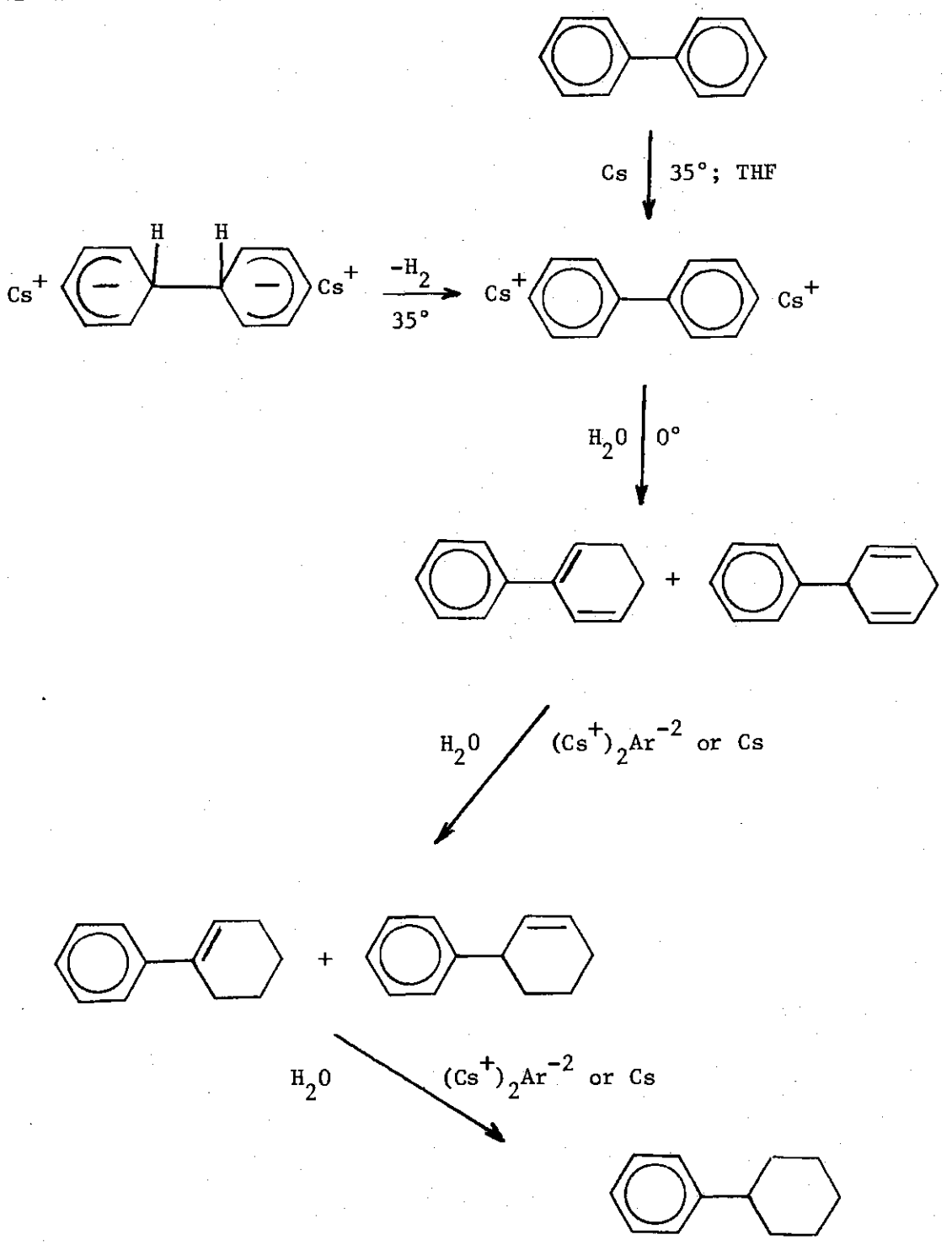
[26]R. G. Kooser, W. V. Volland, and J. H. Freed, J. Chem. Phys., 50, 5243 (1969).

[27]G. L. Mallinoski, W. H. Bruning, and R. G. Griffin, J. Amer. Chem. Soc., 92, 2665 (1970).

[28]Reference 4, p. 226.

[29]R. G. Lawler and C. T. Tabit, J. Amer. Chem. Soc., 91, 5671 (1969).

Scheme 5

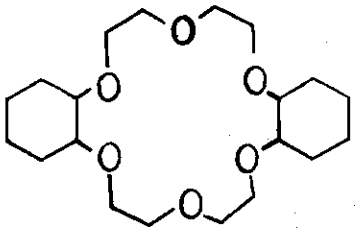

Cs
35°; THF
H
H
Cs+
Cs+
-H2
35°
Cs+
Cs+
H2O
0°
+
H2O
(Cs+)2Ar-2 or Cs
+
H2O
(Cs+)2Ar-2 or Cs

the benzene radical anion. Thus for the reaction:

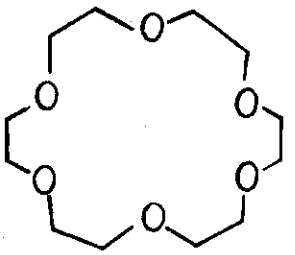
$$Ar^{\cdot-} + C_6H_6 \underset{\text{DME}\ -100°}{\overset{\text{Na-K}}{\rightleftharpoons}} Ar + C_6H_6^{\cdot-}$$

the aromatic hydrocarbons were found to have the following equilibrium constants (decreasing order of electron affinities): benzene, 1 > toluene, 4.4 > p-xylene, 9.1 > ethylbenzene, 22 > cumene, 40 > m-xylene, 51 > t-butylbenzene, 110 > p-diethylbenzene, 120 > p-diisopropylbenzene, 629 > o-xylene, 890 > p-di-t-butylbenzene, > 4300.

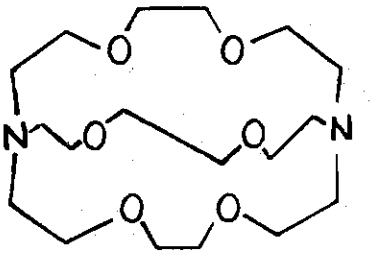
Dye[30] has reported the solubilization of potassium and cesium metals in THF and ether through the use of dicyclohexyl-18-crown-6. With both solvents, deep blue solutions were formed. Solutions of both potassium and cesium were readily formed in THF at room temperature and were stable for several hours even in the absence of excess metal. While THF solutions were stable for several days at -78°C, the solutions in diethyl ether were stable for hours at -78°C or for 5-10 minutes at room temperature. Metal concentrations of approximately 1 x 10^{-4}M were obtained by using 5 x 10^{-3}M solutions of dicyclohexyl-18-crown-6. Komarynisky and



dicyclohexyl-18-crown-6



18-crown-6



[2.2.2]cryptate

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[30]J. L. Dye, M. G. DeBacker, and V. A. Nicely, J. Amer. Chem. Soc., 92, 5226 (1970).

Weissman[31] have reported the preparation of the radical anions of benzene and toluene in parent solvents using dicyclohexyl-18-crown-6 in contact with a potassium mirror. Kaemph[32] has reported that dissolution of sodium, potassium, rubidium, and cesium in benzene and toluene in the presence of either 18-crown-6 or the [2.2.2]cryptate to form the corresponding radical anions. The interaction between the encapsulated cation and the radical anion was weaker when the cryptand was used. Nelson and Zelewsky[33] reported that the contact of benzene, toluene, and mesitylene solutions of 18-crown-6 with cesium and potassium mirrors gave the corresponding radical anions. Since sodium mirrors did not react to give radical anions, they questioned the purity of the sodium used by Kaemph and suggested that it was contaminated with potassium. In related work, it has been shown that potassium reacts with benzene in the presence of polyethylene oxide to give a red benzene radical anion solution.[34] Irradiation of this solution with UV-light or direct sunlight results in a green solution of the diphenyl radical anion. When the benzene was distilled from the red benzene radical anion solution and replaced with THF, the diphenyl radical anion was formed. However, the reaction of potassium with benzene in the presence of polyethylene oxide in THF gave only the red solution. Hart[35] has shown that irradiation of alkaline

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[31] M. A. Komarynsky and S. I. Weissman, J. Amer. Chem. Soc., 97, 1589 (1975).

[32] B. Kaemph, S. Raynal, A. Collet, F. Schue, S. Boileau, and J-M. Lehn, Agnew. Chem. Internat. Edit., 13, 611 (1974).

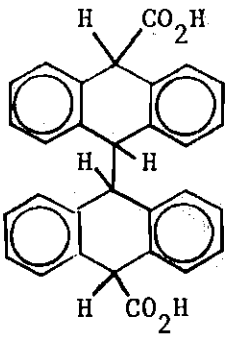
[33] G. V. Nelson and A. von Zelewsky, J. Amer. Chem. Soc., 97, 6279 (1975).

[34] I. M. Panayotov, D. T. Petrova, and C. B. Tsvetanov, Makromol. Chem., 176, 815 (1975).

[35] M. H. Studier and E. J. Hart, J. Amer. Chem. Soc., 91, 4068 (1969).

solutions with γ-rays generates hydrated electrons which react with benzene to give 1,4-dihydrobenzene and other reduction products including dimeric products of largely unknown structure from $C_{12}H_{10}$ to $C_{12}H_{22}$.

Winkler and Winkler[36] have found that at relatively high concentrations of lithium anthracide (2×10^{-2}M) in diethyl ether a solid precipitated which on hydrolysis gave 9,9',10,10'-tetrahydro-9,9-dianthryl. This shows that the radical anion of anthracene may have both radical and anion character as postulated by Schlenk and Bergmann[37] who, on carbonation of a concentrated solution of anthracene radical anion found a diacid of the following structure. However since they also erroneously claimed



isolating an analogous dimer from the reaction of sodium with phenathrene, Holly in his review of this work was therefore skeptical of these results.[3]

Gerson and coworkers[38,39] have found that, while the radical anions of bibenzyl, paracyclophanes, and diphenylmethane in etheral solvents are stable for hours at low temperatures, the radical anion of

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[36] H. J. S. Winkler and H. Winkler, J. Org. Chem., 32, 1695 (1967).

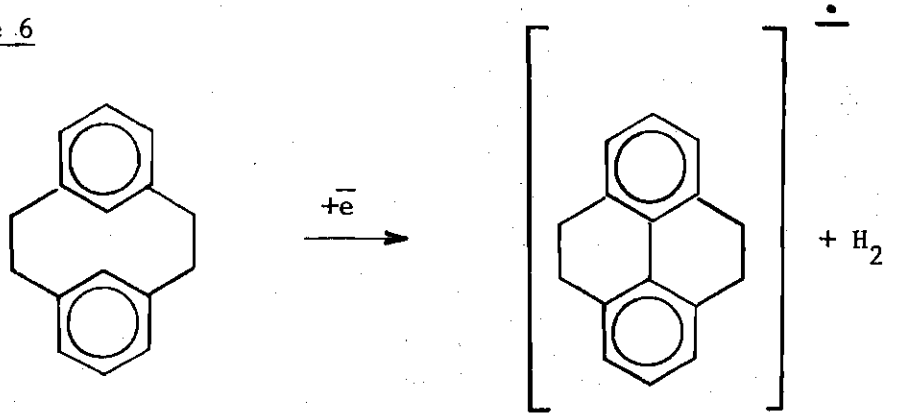
[37] W. Schlenk and E. Bergmann, Ann., 83 (1928).

[38] F. Gerson and W. B. Martin, Jr., J. Amer. Chem. Soc., 91, 1883 (1969).

[39] C. Elschenbroich, F. Gerson, and V. Boekelheide, Helv. Chim. Acta, 58, 1245 (1975).

[2.2]metacyclophane undergoes chemical conversion even at -80°C to -100°C. Thus the ESR spectrum obtained on the reduction of [2.2]metacyclophane by potassium were identical with that of the radical anion of 4,5,9,10-tetrahydropyrene (see Scheme 6).

Scheme 6



Alkali metals could also react with alkylbenzenes in the same manner as diphenylmethane and triphenylmethane to first form a radical anion and then replace an acidic hydrogen to form a benzylic anion. However, this has not been observed for the alkali metals lithium, sodium, or potassium. Cesium however does react with toluene at 28.5°C (the melting point of cesium) to form benzyl cesium.[40] Hackspill[10] reports that xylene, ethylbenzene, cumene, and tetrahydronaphthalene all form benzylic carbanions. These were isolated and identified after carbonation

Scheme 7

[40] J. dePostis, Compt. rend., 222, 398 (1946).

and acidification as the corresponding organic acids. Collingnon[41] has shown that at 20°C in the presence of THF toluene, ethylbenzene, cumene, xylenes, and mesitylene are directly metallated by cesium with quantitative evolution of hydrogen. The relative rates of reaction (these rates are not statistically corrected for the number of benzylic hydrogens) for these hydrocarbons with cesium to form carbanions were found to be: o-xylene, 1.00 > toluene, 0.43 > m-xylene, 0.34 > mesitylene, 0.32 > ethylbenzene, 0.16 > p-xylene, 0.04 > cumene, 0.03.

Ziegler[42] has shown that dissociable ethanes such as tetraphenylethane react with liquid sodium-potassium alloy to form diphenylmethylpotassium[11] which after hydrolysis gave diphenylmethane and after carbonation diphenylacetic acid. However, Conant and Garvey[43] found that dibenzyl did not cleave when reacted with sodium-potassium alloy in either ether or benzene. Gilman and Young[11] found that bibenzyl reacted with potassium-rubidium alloy in petroleum ether to give after carbonation sym-diphenylsuccinic acid. Pearson and coworkers[44] found that the radical anions of diarylethanes and [2.2]paracyclophane prepared by reaction of the hydrocarbon with a potassium mirror in THF or DME at -78°C decompose on warming to diamagnetic highly colored species. Quenching of the highly colored decomposition products of the radical anions of

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[41] N. Collingnon, J. Organometal. Chem., 96, 139 (1975).

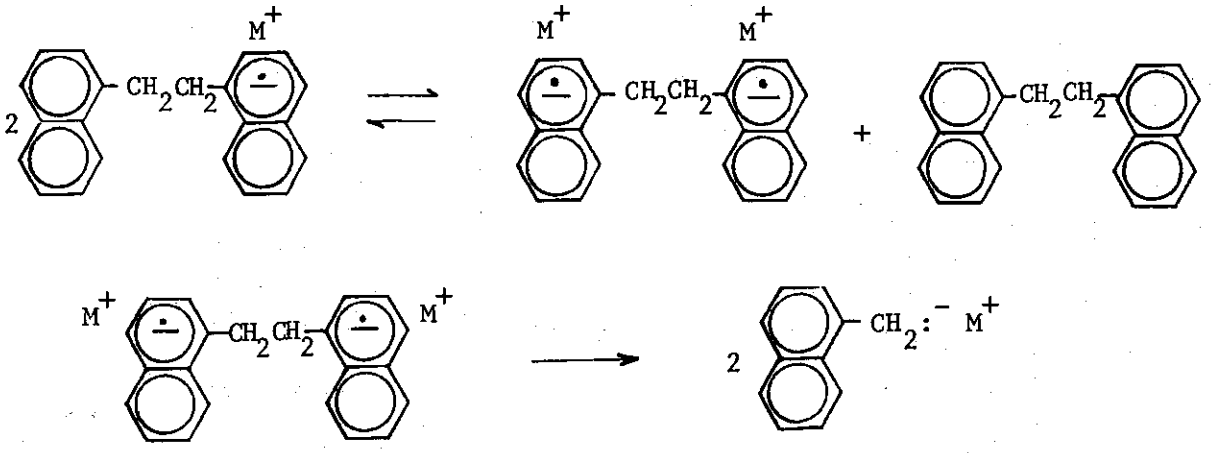
[42] K. Ziegler, Chem. Ber., 568, 1740 (1923).

[43] J. B. Conant and B. S. Garvey, Jr., J. Amer. Chem. Soc., 45, (1923).

[44] J. M. Pearson, D. J. Williams, and M. Levy, J. Amer. Chem. Soc., 93, 5478 (1971).

bibenzyl, 1,2-di-α-naphthylethane, and 1,2-di-9-anthrylethane with methanol gave toluene, 1-methylnaphthalene, and 9-methylanthracene respectively (no yields were given). The optical spectra of the decomposition products of the radical anions of 1,2-di-α-naphthylethane and 1,2-di-9-anthrylethane were shown to be identical to the carbanions formed by the cleavage of α-methoxymethylnaphthalene and 9-methyoxymethylanthracene with potassium. Marshall and Folsom[45] found that when a solution of [2.2]paracyclophane in THF was added to sodium in refluxing ammonia and then protonated with alcohol a 94% yield of p,p'-dimethylbibenzyl was obtained. It has been shown by Lagendisk and Szwarc that for 1,2-di-α-naphthylethane compounds reaction in etheral solvents with alkali metals or lithium bibphenylide generates first the radical anion and then the diradical anion which cleaves to form two equivalents of α-naphthylmethyl anion (see Scheme 8).[46]

Scheme 8



[45] J. L. Marshall and T. K. Folsom, Tetrahedron Lett., 757 (1971).

[46] A. Lagendijk and M. Szwarc, J. Amer. Chem. Soc., 93, 5359 (1971).

Since only cesium of all the alkali metals reacts extensively with benzene to form a high yield of radical anion and subsequently the dianionic benzene dimer, cesium (or low melting cesium alloys) is the alkali metal best suited for the low temperature study of the dimerization of alkyl benzenes, intramolecular cyclization of polyphenyl alkanes, and cleavage or intramolecular cyclization of bibenzyl type compounds. Thus it is the purpose of this research in part to improve the yield of the benzene dimer from the reaction of cesium with benzene[47] (see Scheme 4) through the use of the low melting Cs-K-Na alloy and to determine if similar dimerization reactions occur in the low temperature reactions of toluene,[47] m-xylene, p-xylene and t-butylbenzene with Cs-K-Na alloy in THF. The reactions of 1,3-diphenylpropane, bibenzyl, 1,2-di-p-tolylethane, 2,3-dimethyl-2,3-diphenylbutane and 1,2,2-triphenylpropane with Cs-K-Na alloy were investigated to determine if intramolecular cyclization, cleavage or reduction would occur in these systems. The reactions of benzene, biphenyl, 2,2-diphenylpropane, 1,3-diphenylpropane, and cyclohexyl chloride with Cs-K alloy were studied to establish whether or not cesium was the reacting metal in this binary alloy. Similarly the reaction of benzene,[47] toluene,[47] 1,3-diphenylpropane, 1,1,1-triphenylethane,[47] and 2,2,3-triphenylpropyl chloride with Cs-K-Na alloy were investigated to determine the reacting metal in the ternary alloy. In addition, the effect of addition of 18-crown-6 on the reactions of benzene with cesium and Cs-K-Na alloy and of m-xylene with Cs-K-Na alloy were studied.

A preliminary communication abstracting the reactions of benzene,

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[47] E. Grovenstein, Jr., T. H. Longfield, and D. E. Quest, J. Amer. Chem. Soc., 99, 2800 (1977).

toluene, and 1,1,1-triphenylethane with Cs-K-Na alloy from this thesis and the reaction of benzene with cesium metal from the Ph.D. thesis of T. H. Longfield[4] has been published.[47]

CHAPTER II

REAGENTS AND SOLVENTS

Acetone-d_6

MSD Isotopes perdeuteroacetone, 99.5%, containing 1% by volume of tetramethylsilane was used as an nmr solvent.

Acetonitrile

Fisher Certified A.C.S. acetonitrile was used.

Barium

Fisher barium metal, 99%, lumps were machined into Ba ribbon by Mr. Ken Williams, and stored under heavy mineral oil.

Benzene

Fisher Certified A.C.S. Spectrananalyzed benzene, gc pure, was dried over Na wire before use.

Benzene-d_6

Mallinckrodt perdeuterobenzene, 99.5%, with 1% by volume tetramethylsilane added was used as an nmr solvent.

Benzoic Acid

Unlabeled benzoic acid, gc pure, was used.

2-Benzyl-2,3-Diphenylpropanoic Acid

This acid was prepared by R. E. Williamson by the saponification of the corresponding methyl ester in refluxing alcoholic KOH.

Bibenzyl

Eastman bibenzyl, gc pure, was used.

Biphenyl

Eastman biphenyl, gc pure, was used.

2-Biphenylcarboxylic Acid

Aldrich 2-biphenylcarboxylic acid, gc pure, was used.

4-Biphenylcarboxylic Acid

Aldrich 4-biphenylcarboxylic acid, gc pure, was used.

p,p'-Biphenyldicarboxylic Acid

K and K Laboratories p,p'-biphenyldicarboxylic acid, gc pure, was used.

1,2-Bis(2-Chloroethoxy)Ethane

Eastman Practical Grade 1,2-Bis(2-Chloroethoxy)Ethane was used.

t-Butanol

Fisher Certified A.C.S. t-butanol was used.

t-Butylbenzene

Aldrich t-butylbenzene, 98% pure by gc, dried over Na wire was used.

Carbon Disulfide

Baker Analyzed Reagent carbon disulfide with 1% by volume tetramethylsilane added was used as an nmr solvent.

Carbon Tetrachloride

Fisher Certified A.C.S. carbon tetrachloride with 1% by volume tetramethylsilane added was used as an nmr solvent.

Cesium

MSA Research Corp. cesium metal, 99.9%, in sealed glass ampules under argon was used.

Chloroform-d

MSD Isotopes perdeuterochloroform, 99.8%, with 1% by volume tetramethyl-silane added was used as an nmr solvent.

18-Crown-6

The 18-crown-6 was prepared and purified by the method of Cram and Liotta.[48]

1,3-Cyclohexadiene

Matheson, Coleman & Bell 1,3-cyclohexadiene, gc pure, was used.

Cyclohexane

Baker GC-Spectrophotometric Quality cyclohexane, was used.

Cyclohexanecarboxylic Acid

Eastman cyclohexanecarboxylic acid, gc pure, was used.

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[48] G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, J. Org. Chem., 39, 2445 (1974).

Cyclohexene

Phillips 66 cyclohexene, 99%, distilled on a spinning band column by A. J. Mosher was used.

Cyclohexyl Chloride

Eastman cyclohexyl chloride, gc pure, was used.

Deuterium Oxide

Stock D_2O shown to be 99.5% pure by nmr was used as a quenching reagent.

2,3-Dichloro-5,6-Dicyano-1,4-Benzoquinone (DDQ)

Aldrich DDQ, 98%, was stored in a refrigerator until use.

Dicyclohexyl

Aldrich dicyclohexyl, gc pure, was used.

1,4-Dihydrobenzene

Aldrich 1,4-dihydrobenzene, gc-nmr pure, was used.

1,4-Dihydrobiphenyl

This compound prepared by Longfield[49] was 90% pure by gc.

2,3-Dimethylbenzoic Acid

Aldrich 2,3-dimethylbenzoic acid, gc pure, was used.

2,4-Dimethylbenzoic Acid

Aldrich 2,4-dimethylbenzoic acid, gc pure, was used.

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[49] Reference 4, p. 111.

2,5-Dimethylbenzoic Acid

Aldrich 2,5-dimethylbenzoic acid, gc pure, was used.

2,6-Dimethylbenzoic Acid

Aldrich 2,6-dimethylbenzoic acid, gc pure, was used.

3,4-Dimethylbenzoic Acid

Aldrich 3,4-dimethylbenzoic acid, gc pure, was used.

3,5-Dimethylbenzoic Acid

Aldrich 3,5-dimethylbenzoic acid, gc pure, was used.

2,2'-Dimethylbiphenyl

K and K Laboratories 2,2'-dimethylbiphenyl, gc pure, was used.

3,3'-Dimethylbiphenyl

Aldrich 3,3'-dimethylbiphenyl, gc pure, was used.

4,4-'Dimethylbiphenyl

Aldrich 4,4'-dimethylbiphenyl, gc pure, was used.

2,3-Dimethyl-2,3-Diphenylbutane

Chem Samples 2,3-dimethyl-2,3-diphenylbutane, 99%, was used.

α,α-Dimethylphenylacetic Acid

K and K Laboratories α,α-dimethylphenylacetic acid, gc pure, was used after being vacuum sublimed (140°C, 1 mm Hg) and recrystallized from hexane.

Diphenic Acid (o,o-biphenyldicarboxylic acid)

Aldrich diphenic acid, gc pure, was used.

Diphenylacetic Acid

Aldrich diphenylacetic acid, gc pure, was used.

1,1-Diphenylethane

K and K Laboratories 1,1-diphenylethane was used.

Diphenylmethane

Eastman Practical Grade diphenylmethane 94% (6% fluorene) pure by gc was used. This compound was vacuum distilled (87°C, 0.1 mm Hg) before use.

1,3-Diphenylpropane

This compound was prepared by the Wolff-Kishner reduction[50] of sym-diphenylacetone and was vacuum distilled (78°C, 0.2 mm Hg) before use.

2,2-Diphenylpropane

Aldrich 2,2-diphenylpropane, 95% was stored over 4 Å molecular sieves.

2,2-Diphenylpropionic Acid

Aldrich 2,2-diphenylpropionic acid, gc pure, was used.

1,2-Di-p-Tolylethane

Aldrich 1,2-Di-p-Tolylethane, gc pure, was used.

Ethylbenzene

Matheson ethylbenzene, Coleman and Bell, gc pure, was used.

Ethyl Benzoate

Eastman ethyl benzoate, 95% pure by gc, was used.

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[50] H. Minlon, J. Amer. Chem. Soc., 68, 2487 (1946).

Ethyl Ether

Fisher Anhydrous Grade ethyl ether was used.

Flourene

Eastman flourene, 90% pure by gc, was used.

Hydrochloric Acid

Fisher Reagent A.C.S. hydrochloric acid, was used.

Iodine

Mallinkrodt U.S.P. resublimed iodine crystals were used.

m-Iodotoluene

Eastman reagent grade m-iodotoluene was used.

Isophthalic Acid

Eastman isophthalic acid, gc pure, was used.

Isopropyl Alcohol

Stock isopropyl alcohol was used with crushed dry ice for cooling baths.

Magnesium

Fisher Mg rods were freshly milled into small pieces (ca. 1x5 mm) by Mr. Ken Williams. The milled Mg, because of its very clean surface, was quite reactive and readily formed Grignand reagents.

Magnesium Sulfate

Fisher Anhydrous grade magnesium sulfate was used.

Methanol

Stock methanol was used as the cooling liquid in the Lauda K2/R cooling pump.

1-Methyl-1,4-cyclohexadiene

Chem Samples 1-methyl-1,4-cyclohexadiene, 99%, was used.

2-Methylcyclohexanone

Eastman reagent grade 2-methylcyclohexanone was used.

1-Methylcyclohexene

Chem Samples methylcyclohexene, 99% was used.

Methylene Chloride

Fisher Certified A.C.S. methylene chloride was used.

Methyl Phenylacetate

J. T. Baker methyl phenylacetate, gc pure, was used.

Mineral Oil

Fisher Laboratory Grade mineral oil was used.

Nitrogen

Linde Prepurified nitrogen (5 ppm H_2O max.; 3 ppm O_2 max.) was used.

5% Palladium on Carbon

Engelhard Pd/C was used.

Phthalic Acid

Matheson, Coleman and Bell phthalic acid, gc pure, was used.

Phenylacetic Acid

J. T. Baker phenylacetic acid, gc pure, was used.

4-Phenylbutyric Acid

Eastman 4-phenylbutyric acid, gc pure, was used.

Phenylcyclohexane

Chem Samples phenylcyclohexane, 99% was used.

1-Phenylcyclohexene

Chem Samples phenylcyclohexene, 99%, was used.

p-Phenylenediacetic Acid

Aldrich p-phenylenediacetic acid, gc pure, was used.

Potassium

Fisher potassium sticks were stored under heavy mineral oil.

Potassium Hydroxide

Fisher potassium hydroxide pellets were used.

Sodium

J. T. Baker Purified sodium lump stored under mineral oil.

Sodium Aluminum Hydride

Alpha Inorganics $NaAlH_4$, stored under nitrogen, was used.

Sodium Chloride

Stock U.S.P. NaCl was used.

Sodium Hydroxide

Fisher Certified A.C.S. sodium hydroxide electrolytic pellets were used.

Sodium Tetraphenylboron (NaTPB)

Fisher Reagent Grade sodium tetraphenylboron was used.

Terephthalic Acid

Eastman terephthalic acid, gc pure, was used.

Tetradecane

Aldrich tetradecane, gc pure, was used.

Tetrahydrofuran (THF)

Fisher Certified THF was used after being stored over Na wire and distilled from $NaAlH_4$ while under nitrogen.

Tetramethylsilane (TMS)

MSD Isotopes TMS was used as internal nmr standard.

Toluene

Fisher Certified A.C.S. grade toluene was used after being dried over Na wire.

p-Toluenesulfonic Acid

J. T. Baker reagent grade p-toluenesulfonic acid, was used.

p-Tolyacetic Acid

Aldrich p-Tolyacetic acid, gc pure, was used.

Triethylene Glycol

Fisher Purified grade triethylene glycol was used.

2,2,4-Triphenylbutanoic Acid

This compound prepared by Williams[51] was gc pure.

3,3,4-Triphenylbutanoic Acid

This compound prepared by Williams[51] was gc pure.

1,1,1-Triphenylethane

This compound was prepared by the method of Gomberg and Cone[52] and was found to be pure by gc (R. Carter).

1,2,2-Triphenylpropane

This compound was prepared by the method of Ziegler[53] and was found to be pure by gc (E. Grovenstein, Jr., p. II-47).

1,2,3-Triphenylpropane

This compound was prepared by the method of Hall et al.[54] and was found to be gc pure (R. E. Williamson, p. I-79).

1,1,3-Triphenylpropane

This compound prepared by Williams[51] was gc pure.

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[51] L. P. Williams, Ph.D. Thesis, "Rearrangement of Hydrocarbon Carbanions." Georgia Institute of Technology, 1962, pp. 42-45.

[52] M. Gomberg and L. H. Cone, Chem. Ber., 39, 1466 (1906).

[53] K. Ziegler, Ann. Chem., 437, 244 (1929).

[54] S. S. Hall, S. D. Lipsky, F. J. McEnroe, and A. P. Bartels, J. Org. Chem., 36, 2588 (1971).

2,2,3-Triphenylpropyl Chloride

This chloride was prepared by the method of Grovenstein and Wentworth[55] (R. E. Williamson, p. I-89).

m-Xylene

Phillips Research Grade m-xylene, 99.98%, was used.

p-Xylene

Phillips Pure Grade p-xylene, 99%, was used.

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[55] E. Grovenstein, Jr. and G. Wentworth, J. Amer. Chem. Soc., 89, 1852 (1967).

CHAPTER III

INSTRUMENTATION AND GENERAL PROCEDURES

Proton magnetic resonance spectra (^{1}H NMR) were run on a 60 mHz Varian, A-60D and 60 mHz Varian, T-60 relative to internal tetramethylsilane (TMS). Carbon 13 nuclear magnetic resonance spectra (^{13}C NMR) were run on a Jeol, PFT-100 Fourier Transform NMR Spectrometer relative to internal tetramethylsilane. Electron spin resonance spectra were obtained on a Magnion ESR Spectrometer at X Band (ca 9600 mHz). A solution of 2,2-diphenyl-1-picrylhydrazyl (free radical) in tetrahydrofuran was used as the standard to determine the radical concentration of samples studied. Infrared spectra were run on a Perkin-Elmer, model 237B, grating spectrophotometer and calibrated with the 1600 cm^{-1} band of polystyrene. Ultraviolet-visible spectra were obtained upon a Cary-14 spectrophotometer and Perkin-Elmer 202 spectrophotometer.

Mass spectra were run on a Varian model A-66 and a Hitachi-Perkin-Elmer, model RMU-7L. Peak heights were determined relative to the most intense ion (100%) by use of a Gerber variable scale.

A Jarrel Ash Atomic Absorption-Emission Spectrophotometer, equipped with a hydrogen burner, was used in the flame emission mode at 4044 Å for K, 4556 Å for Cs, and 5890 Å for Na to determine the amounts of these metals in Cs-K-Na alloy samples. The amount of each metal was determined by comparing aqueous solutions of the alloy with standard solutions of varied but known concentration prepared from the appropriate

metal chloride. Melting point determinations were made with use of a Mel-Temp apparatus; only corrected values are reported in this thesis.

Gas chromatography (gc) was accomplished on a Perkin-Elmer Chromatograph (PE), model 881, and an F and M Research Chromatograph (FM), model 810. Stainless steel injector blocks and columns were used with nitrogen as the carrier gas. Both instruments were equipped with hydrogen-flame ionization detectors. The columns used and typical operating conditions are given in Table 1. Gas chromatograms were analyzed by determining the area of the peaks by counting the chart paper squares. Qualitative gc yields are given in relative peak areas whereas absolute or quantitative gc yields are based on an internal standard and known samples.

In all of the reactions of aromatic hydrocarbons or alkyl chlorides with Cs-K or Cs-K-Na alloy, the experiments were carried out in a glove box under a prepurified nitrogen atmosphere. The apparatus normally consisted of either a 4- or 5-necked creased Morton flask fitted with a Morton high-speed stainless steel stirrer, a Friedrich condenser, a thermometer well, and a 4-mm bore Teflon stopcock fitted with a septum. A nitrogen source was connected to the reaction vessel through a mercury bubbler.

The reaction procedure was essentially the same in all experiments. The apparatus was thoroughly flame-dried under a flow of nitrogen. Then the glove box (Lab Con Co., ca 12 ft^3 volume) was sealed and flushed with ca 24 ft^3 or more of prepurified nitrogen until the oxygen content was too low to sustain combustion of a match. After flushing

Table 1. Columns Used in Gas Chromatographic Analysis*

Column I:	6'--1/8"--10% Carbowax 20-M on 60/80 Chromosorb W (180°, 200°, 200°, 3.5, FM)
Column II:	4'--1/8"--3.6% OV-17 on 100/120 Chromosorb W (180°, 225°, 225°, 3.6, PE)
Column III:	12'--1/8"--10% Carbowax 20-M on 100/120 Chromosorb Q (110°, 130°, 145°, 3.0, PE)
Column IV:	12'--1/4"--15% Carbowax 20-M on 60/80 Diatoport-S (170°, 200°, 200°, 2.1, FM)
Column V:	6'--1/4"--10% SE-30 on 60/80 Chromosorb G (170°, 200°, 200°, 2.1, FM)
Column VI:	12'--1/8"--15% FFAP on 100/120 Chromosorb W (80°, 150°, 120°, 3.5, PE)
Column VII:	12'--1/8"--15% FFAP on 100/120 Chromosorb W (80°, 200°, 200°, 2.1, FM)
Column VIII:	6'--1/8"--10% SE-30 on 80/100 Variport (175°, 250°, 220°, 3.5, PE)

*The sequence of numbers given for each column is as follows: oven temperature, injector temperature, detector temperature, flow rate, and the gas chromatograph used.

the glove box, a flask containing tetrahydrofuran (THF) and $NaAlH_4$ (ca. 1 gm) was attached to the condenser and the THF was distilled into the reaction vessel. The cesium alloy was added and the THF and alkali metal were stirred at room temperature for 30 minutes. The reaction mixture was then cooled to the reaction temperature*; and the compound to be reacted, dissolved in THF, was syringed into the flask. During the reactions, samples were taken for further study at various intervals of time. All reactions were carried out with vigorous stirring. The reactions were terminated either by fitting a 0.25 inch glass syphon into the flask and jetting the contents into a flask containing crushed dry ice or by fitting a 12 gauge cannula through the septum equipped stopcock and slowly jetting the contents into a flask containing water or deuterium oxide. (The use of the cannula prevents extra reduction of the products by excess alkali metal since its height can be adjusted to prevent the siphoning of the liquid cesium alloy from the bottom of the reaction flask.)

The samples quenched with Dry Ice were reduced to dryness, dissolved in water and then extracted with ether and then acidified with concentrated HCl. The acids were isolated by extraction with ether, dried ($MgSO_4$) and the ether distilled off through a column. Gas chromatography samples were prepared by esterification with diazomethane.

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*Cooling was achieved by use of crushed Dry Ice/isopanol baths (-80°C) or by use of a special jacketed Morton Flask (see Figure 2) through which cooled methanol was pumped (-45° to room temperature) by a Lauda K/2R thermostatically equipped circulating pump in tandem with a Lauda cold storage vessel (i.e., a 10 Kg Dry Ice/isopanol bath).

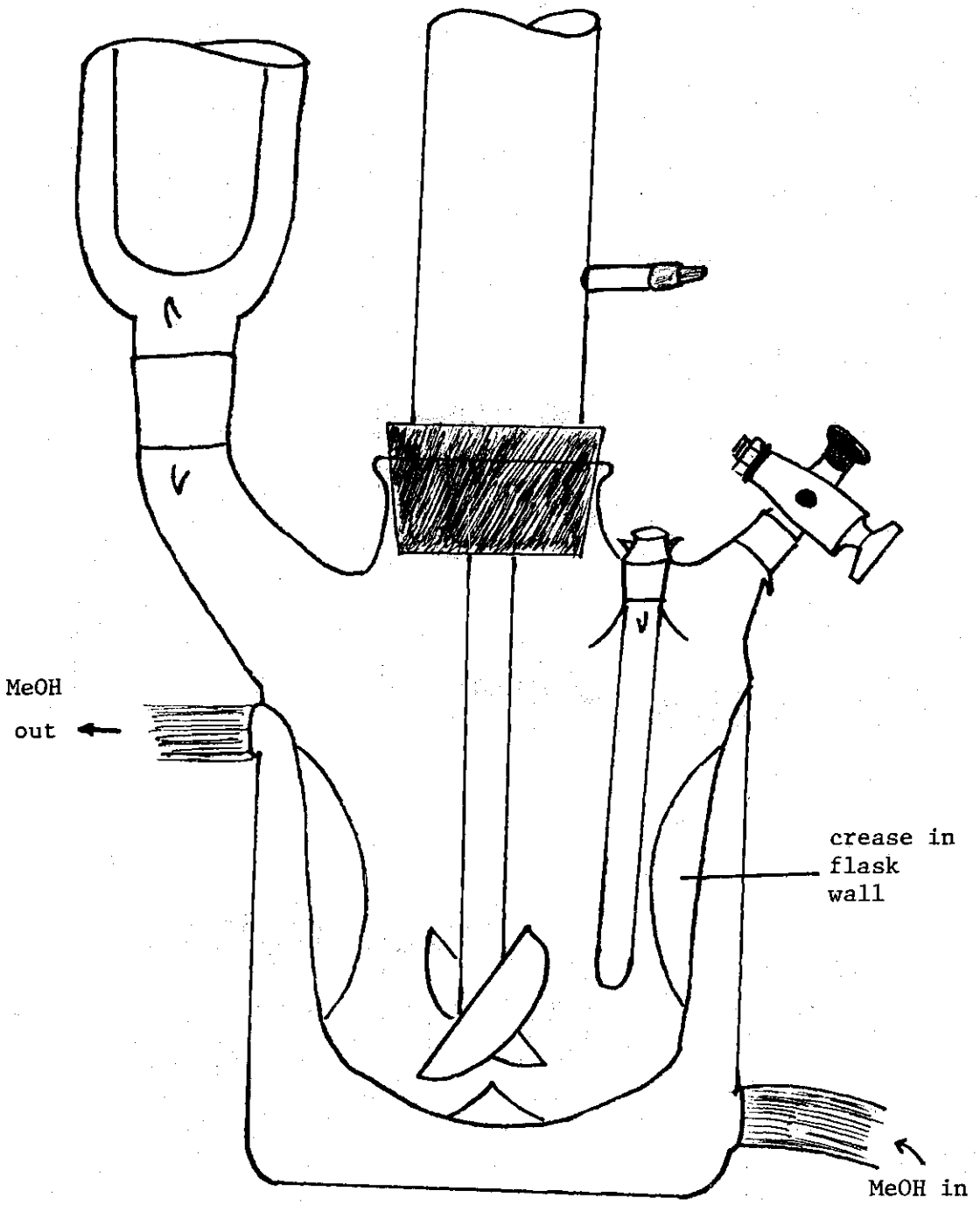

Figure 1. Jacketed Morton Flask.

Samples quenched with H_2O or D_2O were worked up by salting out the organic phase and extracting with three portions of ether. The organic extracts were combined, dried over magnesium sulfate and filtered. The filtrate was either analyzed as is, concentrated to a small volume or concentrated to dryness depending on the expected products.

Analysis of cesium alloys before and after the reaction was carried out in the following manner. The alloy was first allowed to settle out of the reaction mixture. Then a sample was syringed out of the flask and centrifuged. (In low temperature reactions the centrifuge cup contained a slurry of Dry Ice/isopropanol at the reaction temperature.) A sample of clean alloy was then syringed out of the alloy layer at the bottom of the centrifuge tube and placed in a septum and ground glass sealed weighing vial. The sample was weighed and then decomposed with t-butanol and water. The sample was diluted to 100 ml, and aliquots were titrated with standard acid using a platinum tipped microburet to the phenolphthalein end-point to determine the concentration of the hydroxide ion. At this point, the weight of the alloy and mmols of base can be used to calculate the composition of Cs-K alloy. For Cs-K-Na alloy more data is needed to determine the composition. Therefore, additional aliquots were treated with excess aqueous sodium tetraphenylboron, and the potassium and cesium tetraphenylboron were precipitated.[56] The resulting mixture was allowed to stand overnight and then was centrifuged for one hour at 20,000 rpm in a model K International Centrifuge. The

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[56] H. Flashka and A. J. Barnard, Jr., "Advances in Analytical Chemistry and Instrumentation." Vol. 1, Interscience, New York, 1960, pp. 14-29.

supernatant solution was decanted and saved for use as a wash liquid. The white precipitate was then washed into a filter crucible, vacuum filtered, and washed with five ml of distilled water. The precipitate was dried at 100°C overnight, cooled to a constant weight in a dessicator over calcium chloride, and weighed. The composition of Cs-K-Na alloy can be calculated by solving three simultaneous equations for three unknowns (see the Appendix).

CHAPTER IV

EXPERIMENTAL DETAILS

Preparation of Cesium Alloys

Cesium alloys were prepared in a glove-box under a prepurified nitrogen atmosphere in a 100-ml round-bottom flask equipped with a septum and a pyrex coated magnetic stir bar. The cesium metal, in a pyrex ampoule, was melted and decanted into the flask. The potassium and sodium metals were cut from pure metal lumps while under heavy mineral oil. The sodium and potassium cuttings were washed with diethyl ether in the glove-box and were then placed inside the flask. The metals were heated until completely molten and then mixed for two hours. The alloy was transferred via a canula and N_2 pressure to septum-equipped annealed pyrex vials. The vials were then chilled in liquid nitrogen and the necks were sealed using a gas-oxygen torch. The alloy compositions were as follows: Cs-K eutectic (50 atom % K and 50 atom % Cs, fp -37.5°C) for use at room temperature, 70 atom % Cs -30 atom % K for use at -20°C (fp -25°C, however as Cs is extracted from this alloy by the reactant the composition approaches the eutectic fp = -37.5°C), and eutectic Cs-K-Na alloy[2] (47.4 atom % K, 40.8% Cs, and 11.8 % Na; fp -78°C) for use at temperatures as low as -75°C.

Reaction of Benzene with Cs-K Alloy at -20°C; Analysis of Cs-K Alloy for the Reacting Alkali Metal

In experiment II-122*, analysis of a sample of the Cs-K alloy

*The first number is the research notebook and the second is the page.

(0.2543 g ± 0.0002 g; 2.253 ± 0.001 mmol) gave an alloy composition of 78.6 ± 0.2 atom % Cs and 21.4 ± 0.1 atom % K before the addition of benzene. The Cs-K alloy (40.71 mg-atom Cs, 11.05 mg-atom K) in a blue THF (250 ml) solution was cooled to -24°C. At this temperature 1.2983 g (16.62 mmol) of benzene in 5.0 ml of THF was syringed into the flask. There was immediate formation of the cesium benzenide black precipitate; after 77 minutes the flask color was bright green (yellow dicesium 1,1'-dihydrobiphenylide precipitate in a blue solution of dissolved cesium). After 122 minutes of reaction time, at -17°C, a second Cs-K alloy sample (0.5000 ± 0.0002 g; 5.310 ± 0.001 mmol) was analyzed and found to have a composition: 58.5 ± 0.2 atom % Cs and 41.5 ± 0.2 atom % K. At 137 minutes of reaction time, the flask's contents were siphoned into 50 ml of ice water (no care was taken to exclude jetting Cs-K into the water). After standard work-up and gc analysis on a FFAP column (VI, 90°C),* the following monomeric products (mmol yield, mole % yield based on benzene as limiting reagent, gc retention time) were observed: cyclohexene (2.93 mmol, 17.6 mole %, 3.6 min.), 1,4-dihydrobenzene (1.93 mmol, 11.6 mole %, 5.6 min.), and benzene (5.24 mmol, 31.5 mole %, 6.4 min.). On the same basis, analysis for dimeric products by temperature programming a Carbowax 20-M column (IV, 80° for six min. then temperature programmed at 60°/min. to 120°C) gave the following product: 1,1',4,4'-tetrahydrobiphenyl (1.14 mmol, 13.7 mole % yield based on benzene, 18.9 min.). The reaction mixture was reduced on the rotary evaporator to a

*Column number, oven temperature (complete identification of columns is in Table 1).

brown oil (0.5857 g) and vacuum distilled in a Hickman still (60-80°C at 0.4 mm of Hg). The weight of 1,1',4,4'-tetrahydrobiphenyl (92% pure by gc) collected was 0.1830 g which agrees closely with 0.1806 g calculated from the gc data.[57] After this distillation 0.1987 g (15.3 wt. % based on benzene) of nonvolatile residue was recovered.

In experiment, III-145, analysis of a sample of premade Cs-K alloy (0.3568 ± 0.0002 g; 3.271 ± 0.001 mmol) gave an alloy composition of 74.6 ± 0.1 atom % Cs and 25.4 ± 0.1 atom % K before the addition of benzene. The Cs-K alloy (60.09 mg-atom Cs, 20.45 mg-atom K) in the blue THF (250 ml) solution was cooled to -18°C. At this temperature 3.0949 g (39.62 mmol) of benzene was syringed into the flask. The flask color darkened immediately to a black and then to a dark green. After two hours at -18°C, the flask was a bright green color. After four hours of reaction, a second alloy sample (0.4560 ± 0.0002 g, 5.054 ± 0.001 mmol) was removed and the final alloy composition was found to be 54.5 ± 0.1 atom % Cs and 45.5 ± 0.1 atom % K. Then the reaction mixture was carefully jetted into 500 ml of ice water. Care was taken to exclude alloy from this quench, which was completed in thirty minutes. After standard work-up and gc analysis on a FFAP column (VI, 90°C), the following monomeric products (mmol yield; mole % yield based on benzene as limiting reagent; gc retention time) were observed: cyclohexene (1.02 mmol; 2.6 mole %; 4.1 min.), 1,4-dihydrobenzene (4.60 mmol; 11.6 mole %; 6.8 min.), and benzene (7.59 mmol; 19.2 mole %; 7.8 min.). On the same basis, gc

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[57] Reference 4, p. 229. The IR spectrum of this isolated sample of 1,1',4,4'-tetrahydrobiphenyl is reported.

analysis for the benzene dimer on a Carbowax 20-M column (III, 110°C) indicated a high yield of 1,1',4,4'-tetrahydrobiphenyl (11.57 mmol; 58.4 mole %; 11.3 min.).

Reaction of Benzene with Cs-K-Na Alloy at -50°C;
Analysis of Cs-K-Na Alloy for the Reacting Alkali Metal

In experiment III-45, analysis of a sample of Cs-K-Na alloy (0.2811 ± 0.0002 g Cs-K-Na; 3.434 ± 0.001 mmols MOH; 1.2350 ± 0.0020 g of Cs-KTPB) gave an alloy composition of 47.6 ± 0.4 atom % Cs,

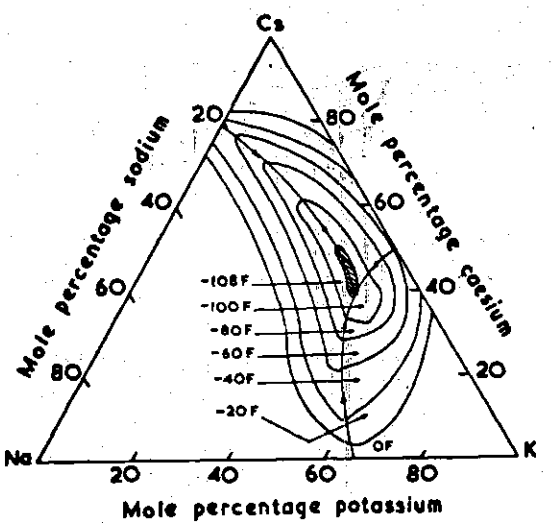

Figure 2. The Sodium-Potassium-Cesium System (molar basis).[2]

40.3 ± 0.3 atom % K, and 12.1 ± 0.2 atom % Na. (Note Figure 2, the above composition's freezing point is -73°C.) The Cs-K-Na alloy (39.84 mg-atom Cs; 33.66 mg-atom K; 10.13 mg-atom Na) in a blue THF (350 ml) solution was cooled to -75°C with vigorous stirring. At this

temperature, 1.2330 g (15.79 mmol) of benzene in 5.0 ml of THF was syringed into the deep blue THF solution. The color changed instantly upon addition from blue to black. The flask was maintained for two hours at -75°C (attempts to sample the alloy failed at this time due to solidification. After the flask was allowed to warm at -50°C for one hour (three hours total reaction time), a second Cs-K-Na alloy sample was analyzed (0.6514 ± 0.0002 g Cs-K-Na; 8.821 ± 0.001 mmols MOH; 3.1300 ± .0020 g of Cs-KTPB) and found to have a composition: 38.9 ± 0.3 atom % Cs, 49.9 ± 0.4 atom % K, and 11.2 ± 0.2 atom % Na. During the sampling, the reaction mixture stood for 45 minutes with no stirring. The flask's black colored contents were then siphoned into 500 ml of ice water. This resulted in a violent explosion as all of the remaining Cs-K-Na liquid alloy jetted into the ice water at one time. Only about 1.0% of the organic products were recovered. After standard work-up and gc analysis on a FFAP column (VI, 70°C) the following monomeric products (mmol; relative mole % yields based on the total mmol equivalents of benzene in the recovered products; retention time) were observed: cyclohexene (0.114 mmol; 59.4 rel. mole %; 3.8 min.), 1,4-dihydrobenzene (0.021 mmol; 10.9 rel. mole %; 6.6 min.), and benzene 0.049 mmol; 25.5 rel. mole %; 7.6 min.). On the same basis, analysis by gc on a Carbowax 20-M column (IV, 115°C) gave the dimerization product: 1,1',4,4'-tetrahydrobiphenyl (0.004 mmol; 4.2 rel. mole %; 11.3 min.).

In reaction III-153, analysis of a sample of premade Cs-K-Na alloy (0.4153 ± 0.0002 g; 5.384 ± 0.01 mmols MOH; 1.969 ± 0.002 g of Cs-KTPB) gave the composition: 42.1 ± 0.3 atom % Cs, 49.0 ± 0.3 atom % K, and 8.9 ± 0.1 atom % Na. (Note Figure 2; this alloy's freezing point is

about -78°C). The Cs-K-Na alloy (40.14 mg-atom Cs, 46.69 mg-atom K, 8.55 mg-atom Na) was vigorously stirred in 250 ml of THF, and this mixture was cooled to -45°C. At this point, 1.0473 g (13.408 mmol) of benzene in 5.0 ml of THF was syringed into the flask. The blue THF solution color instantly changed to black upon the addition. After two minutes the flask color began to turn green and continued to intensify until after one hour the flask color was bright green. At two hours into the reaction, the stirrer was stopped to allow the alloy to settle out. Thirty minutes later, a second alloy sample was analyzed (0.2462 ± 0.0002 g; 3.573 ± 0.01 mmol of MOH; 1.261 ± 0.002 g of Cs-KTPB) and found to have a composition: 33.9 ± 0.3 atom % Cs, 55.7 ± 0.4 atom % K, and 10.4 ± 0.2 atom % Na. After the alloy sampling, three hours of total reaction time, the flask's contents were slowly jetted into 500 ml of ice water. During this quench of the organometallic products care was taken to avoid jetting any alloy into the ice water to avoid overreduction of the products. After standard work-up and gc analysis on a FFAP column (VI, 75°C), the following monomeric products (mmol, mole % yield based on benzene as limiting reagent, gc retention time) were observed: cyclohexene (0.00 mmol; 0.0 mole %; 4.0 min.), 1,4-dihydrobenzene (1.195 mmol; 8.92 mole %; 7.3 min.), and benzene (1.955 mmol; 14.58 mole %; 8.3 min.). On the same basis, the gc analysis for the benzene dimer on a Carbowax 20-M column (IV, 120°) showed a high yield of 1,1',4,4'-tetrahydrobiphenyl (5.075 mmol; 75.7 mole %; 14.8 min.).

In reaction IV-141, Cs-K-Na alloy was reacted with benzene under the same conditions and reaction scale as reaction III-153. After the usual work-up, 80 mg of pure 1,1',4,4'-tetrahydrobiphenyl was isolated by

reducing the reaction mixture under vacuum to a brown oil which was then vacuum distilled in a Hickman still (60-70°C, 0.2 mm Hg). The ^{1}H NMR spectrum ($CDCl_3$) had absorption at δ 2.67 (6.0 H, complex m, allylic) and 5.70 (8.0 H, complex m, vinylic). This is in good agreement with the spectrum reported by Tom Longfield[58] and the ^{1}H NMR spectrum ($CDCl_3$) of 1,4-dihydrobenzene which has absorption at δ 2.67 (4.0 H, s, allylic)* and 5.72 (4.0 H, s, vinylic).* The ^{13}C NMR spectra ($CDCl_3$) of 1,1',4,4'-tetrahydrobiphenyl and 1,4-dihydrobenzene are shown in Figure 3.

Reaction of Cs Sand with Benzene in the Presence of 18-Crown-6

In experiment II-53, 5.7505 g (43.27 mol) of Cs sand was prepared by vigorously stirring the molten metal in 250 ml of refluxing THF for 75 minutes. The stirrer was stopped and the flask was chilled with a dry ice/acetone bath until the flask thermometer read -50°C (the thermometer well was not in contact with the liquid). Then 21.4420 g (274.5 mmol) of benzene was syringed into the flask and the stirrer was restarted. There was an immediate formation of a black precipitate (this was confirmed by centrifugation). After 2.25 hours of reaction time at -75°C, 10.3238 g (39.06 mmol) of 18-crown-6 dissolved in THF was syringed into the flask. Upon addition the color changed from black to red-brown. (A centrifuged sample showed the solution color to be black and the precipitate was red-brown). The reaction was maintained at -75°C for two hours to -5°C. At the higher temperature (-10°C), the flask color was

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[58] Reference 4, p. 64.

*These singlet peaks had about twice the basewidth as the TMS peak.

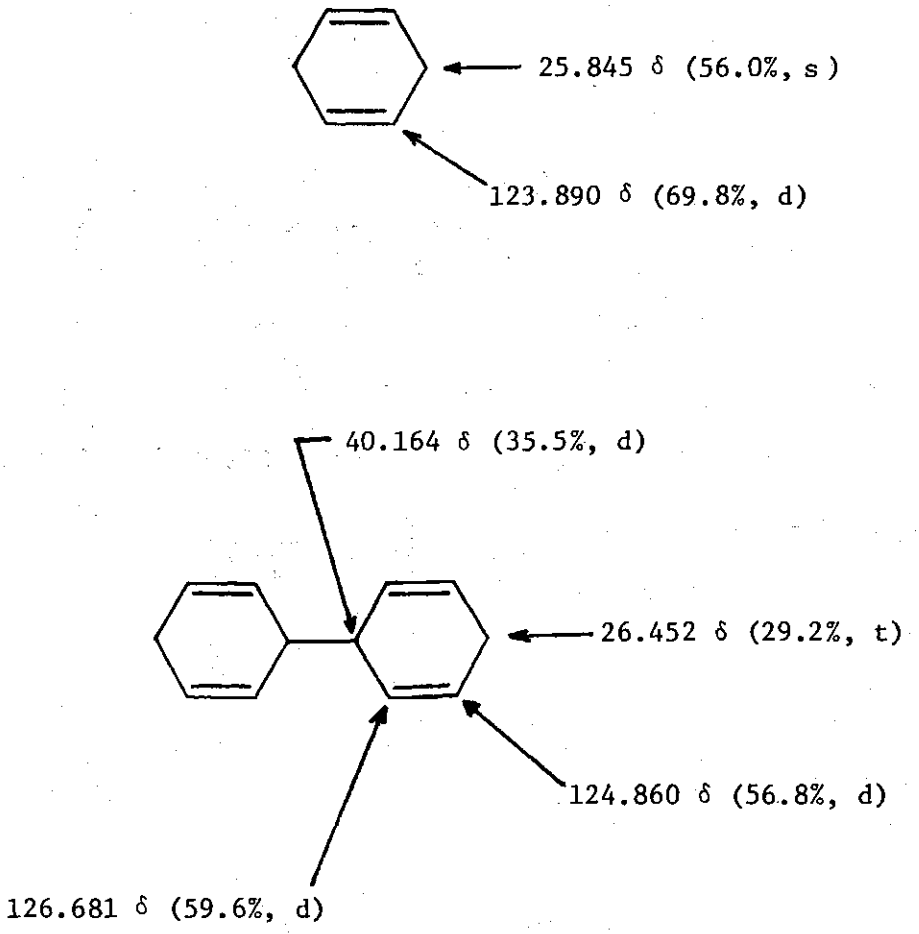

Figure 3. ^{13}C NMR Spectra ($CDCl_3$) of 1,4-Dihydrobenzene and 1,1',4,4'-Tetrahydrobiphenyl with Suggested Assignments for the Absorption Peaks.

bright red (deep red precipitate in a bright red solution). The reaction mixture was then siphoned into 500 ml of ice water. Both the quench products and 5.0 ml samples which were protonated during the course of the reaction were subjected to gc analysis for monomers on a FFAP column (VI, 95°C) and dimer on a Carbowax 20-M column (IV, 135°C) is summarized in Table 2.

In experiment II-157, 5.4686 g of (41.15 mg-atom) of cesium sand was prepared by vigorously stirring the molten metal in 350 ml of refluxing THF for 25 minutes. The flask was then chilled without stirring to -70°C and 10.8777 g (42.08 mmol) of 18-crown-6 dissolved in THF was syringed into the flask. Upon addition and mixing the flask changed immediately to a deep blue color. After 22 minutes of stirring, 3.2140 g (41.85 mmol) of benzene in 5.0 ml of THF was syringed into the flask. The color darkened instantly to black. The reaction was held at -75°C for 3.5 hours with no color change. The reaction temperature was then raised to -30°C; after seven and a half hours total reaction time the flask color began to change from black to brown. Again the reaction temperature was raised to -25°C; after nine and one half hours total reaction time the flask color changed from brown to bright red. At ten and a half hours reaction time, 325 ml of the flask's contents were siphoned into 500 ml of ice water and the other 25 ml was siphoned into partially frozen deuterium oxide. After standard work-up and gc analysis on a FFAP column (VI, 90°C), the following monomeric products (mmol yield, mole % yield based on benzene as limiting reagent, absolute % yield based on cesium as limiting reagent, gc retention time) were observed:

Table 2. Gc Analysis of the Products of the Reaction of Benzene with Cs Sand in the Presence of 18-Crown-6. (monomers column VI, 95°C; dimer column IV, 135°C)

Temperature/Time	Cyclohexene	1,4-dihydrobenzene	1,1',4,4'-tetrahydrobiphenyl
-75°/50 min.	25.3%*(2.74 mmol**)	41.0% (8.87 mmol)	1.0% (0.22 mmol)
-75°/135 min.: added 18-crown-6			
-75°/170 min.	46.2% (5.00 mmol)	14.8% (6.38 mmol)	1.3% (0.28 mmol)
-50°/300 min.	39.2% (4.24 mmol)	33.0% (7.14 mmol)	0.7% (0.17 mmol)
-5°/365 min.: main quench	60.7% (6.57 mmol)	32.9% (7.11 mmol)	2.6% (0.56 mmol)
gc Retention Time	4.0 min.	6.0 min.	18.6 min.

*The absolute yields, based on Cs as limiting reagent, were determined by multiplying the mmol of products times 100% and then the number of Cs needed to achieve the state of reduction and then dividing by 43.27 mg-atoms Cs.

**Mmol yields of the 5 ml gc samples were multiplied by 50 to allow direct comparison with the main quench.

cyclohexene (1.35 mmol, 3.2 mole %, 13.2 absolute %, 2.7 min.), 1,4-dihydrobenzene (11.08 mmol, 26.3 mole %, 53.9 absolute %, 4.1 min.), and benzene (26.14 mmol, 62.0 mole %, 0.0 absolute %, 4.7 min.). On the same basis, gc analysis for the dimeric products on a Carbowax 20-M column (IV, 120°) gave the following products: phenylcyclohexane (0.05 mmol, 0.2 mole %, 0.5 absolute %, 14.8 min.) and 1,1',4,4'-tetrahydrobiphenyl (1.74 mmol, 8.3 mole %, 8.5 absolute %, 16.8 min.).

Mass spectral analysis of the deuterated 1,4-dihydrobenzene (contaminated with THF), isolated by preparative gc had the following peaks in the M^+ ion region, m/e (relative %): 77(14), 78(41), 79(27), 80(36), 81(90), 82(85), 83(10), and 84(1.8). The deuterated product appears to be primarily the dideuterated product M^+ at 82 m/e ($C_6H_6D_2$), from cesium benzenide radical anion. Analysis of a pure sample of 1,4-dihydrobenzene had the following mass spectrum: 37 (3.5), 38 (5.5), 39 (22), 40 (4), 41 (5), 49 (2), 50 (18), 51 (19), 52 (14), 53 (7), 54 (3.7), 62 (1.1), 63 (2.5), 65 (8), 73 (1), 74 (4), 75 (2), 76 (1), 77 (56), 78 (15), 79 (100), 80 (85) M^+, 81 (5.5), and 82 (0.2). The loss of one of the four equivalent allylic hydrogens of $C_6H_8^+$ gives rise to an $(M-1)^+$ ion of 100% relative %. Since in $C_6H_6D_2^+$ there are half as many allylic hydrogens as in $C_6H_8^+$, the intensity of the $(M-1^+)$ ion formed from $C_6H_6D_2^+$ should be 50 relative %. The observed value for this ion is 90 relative %, which may indicate that there is 40 relative % of the $C_6H_7D^+$ molecular ion at m/e 81 in the deuterated products. Hence the ratio of C_6H_7D to C_6H_6D in this sample may be 40: 85. (On this basis, the $C_6H_8^+$ molecular ion is present in a negligible amount.)

Reaction of Cs-K-Na Alloy with Benzene in the Presence of 18-Crown-6

In reaction IV-161, Cs-K-Na alloy (82.9 mg-atoms Cs, 80.8 mg atoms K, 8.6 mg-atoms Na) was vigorously stirred with 350 ml of THF at -43°C. To this deep blue THF solution, 7.4480 g (28.18 mmol) of 18-crown-6 was added. Upon addition of the 18-crown-6, the solution viscosity increased and the blue solution color intensified. After 30 minutes of stirring, 1.0625 g (13.60 mmol) of benzene in 5.0 ml of THF was syringed into the flask. There was no color change or precipitate formation; the reaction mixture was stirred for five hours at -43°C and then siphoned onto crushed dry ice. After standard work-up, 1.2053 g of crude acid was isolated.

^{1}H NMR (C_6D_6) analysis of the crude acid gave the following spectra: δ 3.1 (2.7 H, complex m, allylic), 5.7 (4.0 H, complex m, vinylic), 7.2 (1.8 H, s, aromatic), and 11.0 (1.3 H, s, acidic). This data is consistent with a ratio of 1,4-dihydrobenzoic acid to benzoic acid to tetrahydrobiphenyldicarboxylic acid of 1.4 : 0.6 : 1.0.

For gc analysis, the crude acids were converted to the methyl esters by diazomethane. Since gc separation of benzoic acid from 1,4-dihydrobenzoic acid could not be accomplished on available columns, the esters were aromatized with DDQ (two fold excess DDQ, refluxed in toluene overnight). Gc analysis on a SE-30 column (V, 220°C) and on an OV-17 column (II, 150°C) gave the following aromatized products (mmol, mole % yield based on benzene as limiting reagent, gc retention time on column V, gc retention time on column II) were observed: benzoic acid

(2.29) mmol, 16.8 %, N. A., 2.0 min.), unknown* (0.18 mmol, 1.3 mole %, 0.9 min., 8.5 min.), phthalic acid (0.25 mmol, 1.8 mole %, 1.1 min., 15.2 min.), terephthalic acid (0.25 mmol, 1.8 mole %, 1.2 min., 17.5 min.), unknown** (0.44 mmol, 615 mole %, 1.4 min., 22.5 min.),2-biphenylcarboxylic acid (0.02 mmol, 0.3 mole %, 1.8 min.), 4-biphenylcarboxylic acid (0.02 mmol, 0.3 mole %, 3.0 min.), o,o'-biphenyldicarboxylic acid (0.21 mmol, 3.1 mole %, 3.2 min.), o,p'-biphenyldicarboxylic acid (0.54 mmol, 7.9 mole %, 5.7 min.), and p,p'-biphenyldicarboxylic acid (0.41 mmol, 6.0 mole %, 10.8 min.). Although an authentic gc sample of o,p'-biphenyldicarboxylic acid was unavailable the structure was assigned on the basis of the compound's methyl ester which was isolated by preparative gc. The spectral data is as follows, m/e (relative abundance): 39 (15), 40 (22), 41 (28), 42 (8), 43 (18), 44 (49), 50 (6), 51 (7), 55 (15), 56 (9), 57 (14), 59 (31), 63 (17), 69 (8), 71 (7), 75 (11), 76 (56), 77 (9), 90 (22), 91 (7), 104 (32), 117 (6), 119 (7), 139 (9), 140 (6), 149 (6), 150 (10), 151 (25), 152 (37), 153 (14), 154 (7), 155 (10), 165 (12), 180 (23), 181 (20), 195 (40), 196 (11), 207 (9), 211 (13), 239 (100), 240 (19), 269 (7), 270 (60) M^+, 271 (13), and 272 (3).

This compares favorably with the mass spectra of methyl-o,o'-biphenylcarboxylate, m/e (relative %): 75 (3), 76 (26), 77 (2), 90 (2), 104 (9), 105 (1), 119 (1), 126 (1), 127 (2), 128 (3), 139 (7), 140 (2), 142 (1), 150 (3), 151 (5), 152 (13), 153 (3), 154 (1), 155 (2), 156 (1),

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*Response factor for gc calibration was assumed to be the same as for phthalic acid.

**Response factor for gc calibration was assumed to be the same as for 2-biphenylcarboxylic acid.

165 (5), 166 (2), 167 (3), 168 (6), 169 (2), 179 (1), 180 (14), 181 (3), 195 (9), 196 (17), 198 (3), 211 (100), 212 (18), 213 (2), 239 (4), 240 (1), 270 (2.8) M^+, 271 (0.6), and 272 (0.1), and with the mass spectra of methyl-p,p-biphenyldicarboxylate, m/e (relative %): 75 (9), 76 (48), 77 (7), 80 (5), 81 (3), 82 (5), 84 (3), 90 (20), 91 (5), 95 (5), 97 (5), 104 (32), 105 (4), 106 (4), 119 (5), 126 (3), 127 (7), 141 (5), 150 (8), 151 (14), 152 (38), 153 (8), 154 (4), 155 (8), 156 (3), 165 (9), 166 (4), 167 (4), 168 (3), 169 (3), 179 (7), 180 (3), 181 (3), 183 (3), 196 (6), 211 (4), 239 (100), 240 (19), 241 (2), 269 (1), 270 (48) M^+, 271 (7.5), and 272 (1.0), which were also isolated by preparative gc. The latter two methyl esters have mass spectra identical to that of authentic samples of methyl-o,o'-biphenyldicarboxylate and methyl-p,p'-biphenyldicarboxylate respectively.

Reaction of Toluene with Cs-K-Na Alloy at -45°C

In reaction IV-51, Cs-K-Na alloy (80.7 mg-atoms Cs, 80.8 mg-atoms K, 8.6 mg-atoms Na) was vigorously stirred in 350 ml of THF, and this mixture was cooled to -45°C. Then 2.9936 g (32.49 mmol) of toluene in 5.0 ml of THF was syringed into the flask. The blue solution rapidly darkened with the formation of the black cesium toluenide precipitate. After forty minutes, the flask color was green (yellow precipitate in a blue solution). The reaction was allowed to continue for three hours and then the flask's contents were carefully jetted into 500 ml of ice water. After standard work-up and gc analysis on a FFAP column (VI, 80°C), the following monomeric products (mmol, mole % yield based on toluene as limiting reagent, gc retention time) were observed:

2,5-dihydrotoluene (5.05 mmol, 15.6 mole %, 7.4 min.) and toluene (7.53 mmol, 23.2 mole %, 8.8 min.). On the same basis, analysis by gc on a Carbowax 20-M column (IV, 130°C) gave the dimerization products: 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl (9.65 mmol, 56.3 mole %, 6.4 min.) and an isomeric mixture of 3,3'-dimethyl-1,1',2,4'-tetrahydrobiphenyl and 3,3'-dimethyl-1,1',4,6'-tetrahydrobiphenyl (0.28 mmol, 1.7 mole %, 7.1 min.).

Mass spectral analysis of the 2,5-dihydrotoluene isolated by preparative gc had the following peaks beyond those of the THF contaminant, m/e (relative %): 76 (2), 77 (51), 78 (11), 79 (100), 80 (7), 89 (2), 90 (1), 91 (44), 92 (16), 93 (19), 94 (78) M^+, 95 (9), and 96 (0.5). This spectrum is identical with that of a commercial sample of 2,5-dihydrotoluene.

After the gc analysis, the reaction mixture was reduced under vacuum to 1.7001 g of a yellow oil. The ^1H NMR (CCl_4) of this oil had absorbance at δ 1.66 (3.0 H, s, methyl), 2.53 (3.0 H, complex m, allyl), 5.27 (1.1 H, complex m, vinyl), and 5.60 (1.9 H, complex m, vinyl). This is in good agreement with the structure of 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl and the ^1H NMR ($CDCl_3$) of 2,5-dihydrotoluene which had absorbance at δ 1.65 (3.1 H, s, methyl), 2.57 (4.0 H, s, allyl), 5.40 (1.0 H, s, vinyl)*, and 5.67 (1.9 H, s, vinyl)*. The ^{13}C NMR spectra ($CDCl_3$) of 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl and 2,5-dihydrotoluene are shown in Figure 4. The UV spectrum (95% EtOH) of the oil had an absorbance at 2650 Å, ε = 249.0. The spectrum was repeated, using

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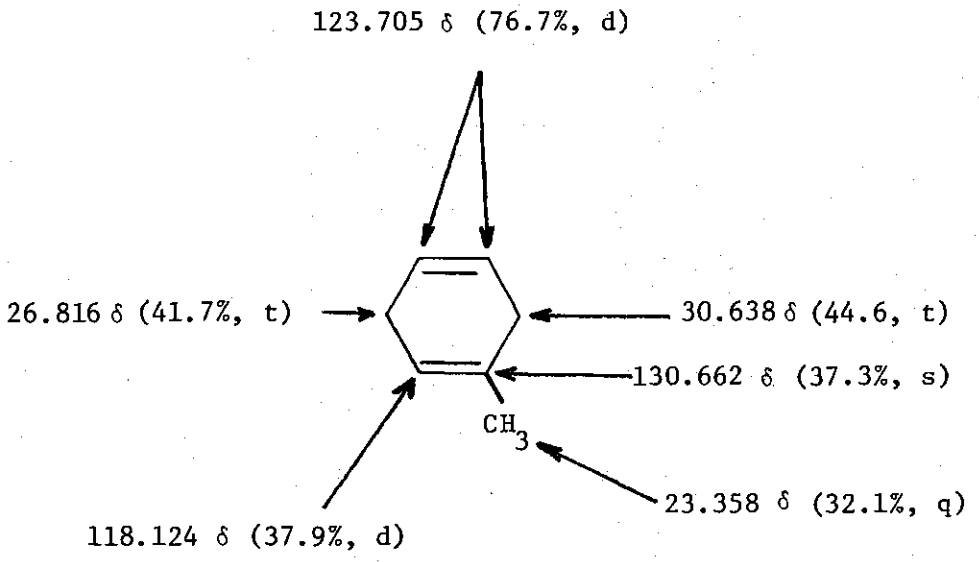
*These singlet peaks have about twice the basewidth as the TMS peak.



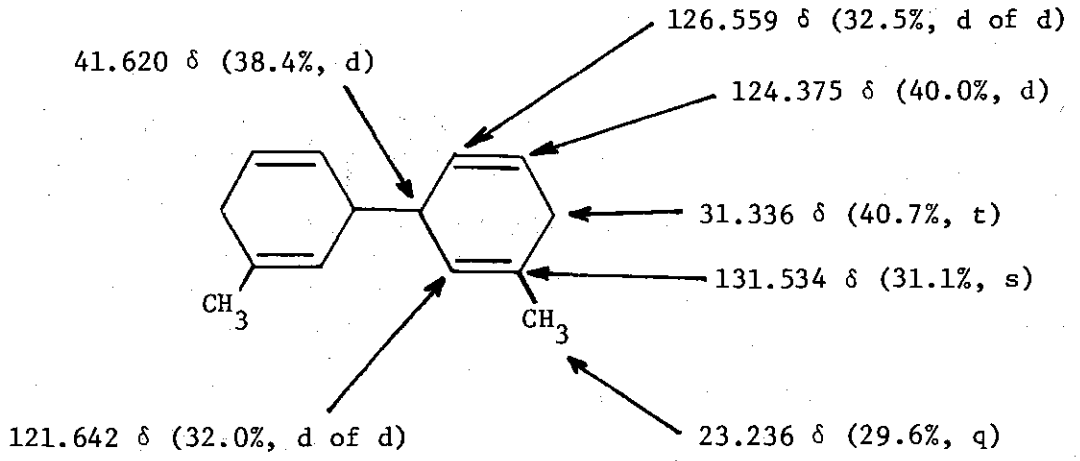


Figure 4. ^{13}C NMR Spectra ($CDCl_3$) of 2,5-Dihydrotoluene and 3,3'-Dimethyl-1,1',4,4'-tetrahydrobiphenyl with Suggested Assignments of Absorption Peaks.

a sample of the 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl isolated by preparative gc, and no absorbance (2650 Å, ε = 0) was observed. Thus about 3 wt. % of the crude dimer has a conjugated diene system. [The UV spectrum (95% EtOH) of 1,3-cyclohexadiene has an absorbance at 2600 Å, ε = 8000.] The IR spectrum of the neat oil had absorbance bands at the following wave numbers (cm^{-1}): 3080 (w), 3025 (s), 2975 (s), 2925 (s), 2875 (s), 2825 (s), 2775 (w), 2710 (w), 1860 (w), 1690 (m), 1640 (w), 1450 (s), 1425 (s), 1380 (s), 1340 (w), 1290 (w), 1240 (w), 1195 (w), 1165 (w), 1145 (w), 1075 (w), 1005 (m), 930 (s), 855 (w), 840 (m), 770 (m), 740 (m), 715 (s), and 650 (m). The mass spectral analysis of the 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl isolated by preparative gc had the following observed spectrum, m/e (relative %): 37 (2), 38 (6), 39 (25), 40 (4), 41 (7), 42 (1), 43 (3), 44 (5), 45 (7), 46 (6), 49 (2), 50 (8), 51 (14), 52 (4), 53 (3), 54 (1), 55 (2), 56 (2), 57 (2), 60 (1), 61 (3), 62 (6), 63 (12), 64 (3), 65 (20), 66 (3), 67 (1), 73 (1), 74 (2), 75 (2), 76 (1), 77 (8), 78 (2), 79 (15), 80 (1), 85 (2), 86 (2), 87 (2), 89 (6), 90 (5), 91 (100), 92 (76), 93 (11), 94 (9), 95 (1), 141 (2), 149 (4), 169 (1), 184 (0.7), 185 (0.4), 186 (1.3) M^+, 187 (0.4), and 188 (0.1). [Mass spectral analysis of the crude oil indicates possible contamination by 3,3'-dimethylbiphenyl (M^+ 182), 1,4-dihydro-3,3'-dimethylbiphenyl (M^+ 184) and m-(3-methylcyclohexyl)toluene (M^+ 188) since the mass spectrum had the following peaks in the M^+ region, m/e (relative %): 181 (0.5, 182 (4.0), 183 (1.5), 184 (5.0), 185 (1.0), 186 (1.5), 187 (1.5), 188 (2.5), 189 (0.8), and 190 (0.5).] The duplicate C, H analysis of the 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl

indicated the compound was 90.44% C and 9.48 % H and 90.46 % C and 9.46 % H. The calculated composition is 90.26% C and 9.74% H.

The ^{1}H NMR solution of the 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl was reduced under vacuum and dehydrogenated overnight by 1 g of 5% Pd/C in 50 ml refluxing toluene. Gc analysis after dehydrogenation on a Carbowax 20-M column (IV, 170°C) gave the following products (relative area %, retention time): 2,2'-dimethylbiphenyl (0.24 rel. area %, 4.9 min.), 2,3'-dimethylbiphenyl (0.14 rel. area %, 7.4 min.), an undehydrogenated compound (3.53 rel. area %, 10.1 min.), and 3,3'-dimethylbiphenyl (96.09 rel. area %, 13.4 min.). The ^{1}H NMR (CCl_4) of the dehydrogenated dimer, which was identical to the ^{1}H NMR of 3,3'-dimethylbiphenyl, had absorbance at δ 2.32 (6.0 H, s, methyl) and 7.12 (8.1 H, complex m, aromatic).

Using an alternate dehydrogenation method, 0.1303 g of the dimer was oxidized overnight by 0.518 g of DDQ in 25 ml of refluxing benzene. The excess DDQ was destroyed by the addition of 1 ml of 1,4-dihydrobenzene. The mixture was filtered and the filtrate was concentrated. The recovered weight of dehydrogenated dimer was 0.1205 g (92.5 wt %). Gc analysis on a Carbowax-20-M column (IV, 170°C) the following products (relative area % yield, retention time) were observed: o,o'-dimethylbiphenyl (0.38 rel. area %, 4.9 min.), o,m'-dimethylbiphenyl (0.19 rel. area %, 7.4 min.), and m,m'-dimethylbiphenyl (99.43 rel. area %, 13.4 min.).

The ^{1}H NMR spectrum (CCl_4) of the product dehydrogenated with DDQ, which was identical to that of authentic 3,3'-dimethylbiphenyl, had absorbance at δ 2.33 (6.0 H, s, methyl) and 7.12 (8.0 H, m, aromatic).

The IR spectrum of this neat oil, which was identical to that of 3,3'-dimethylbiphenyl, had absorbance bands at the following wave numbers (cm^{-1}): 3010 (s), 2930 (shoulder), 2900 (s), 2840 (m), 2710 (w), 1930 (w), 1850 (w), 1760 (w), 1680 (w), 1600 (s), 1575 (s), 1550 (shoulder), 1465 (s), 1445 (shoulder), 1385 (w), 1365 (w), 1155 (w), 1080 (s), 1025 (m), 880 (shoulder), 870 (s), 770 (s), and 690 (s). The UV spectrum (95% EtOH) had a maximum at 2500 Å with ε = 15,900, which was in good agreement with that of authentic 3,3'-dimethylbiphenyl: 2500 Å, ε = 17,500 (literature: 2500 Å, ε = 16,300).[59]

Reaction of Toluene with Cs-K-Na Alloy at -45°C; Analysis of Cs-K-Na Alloy for the Reacting Alkali Metal

In reaction IV-69, analysis of a sample of premade Cs-K-Na alloy (0.2507 ± 0.0002 g Cs-K-Na; 3.012 ± 0.001 mmol of MOH; 1.1385 ± 0.0020 g of Cs-KTPB) gave an alloy composition of 48.3 ± 0.5 atom % Cs, 44.5 ± 0.4 atom % K, and 7.2 ± 0.1 atom % Na. (Note Figure 2, the above composition's freezing point is -73°C.) The Cs-K-Na alloy (43.63 mg-atom Cs; 40.27 mg-atom K; 6.48 mg-atoms Na) in a blue THF (350 ml) solution was cooled to -45°C with vigorous stirring. At this temperature, 1.3630 g (14.79 mmol) of toluene in 5.0 ml of THF was syringed into the flask. The flask color changed instantly upon addition from blue to black. After 45 minutes, the flask color was a dark green (yellow precipitate in a blue solution). After four hours, a second Cs-K-Na alloy sample was analyzed (0.1984 ± 0.0002 g Cs-K-Na; 2.712 ± 0.001 mmol MOH;

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[59]"Ultraviolet Spectral Data." American Petroleum Research Project 44, serial no. 705.

0.9810 ± 0.0020 g Cs-KTPB) and found to have a composition: 37.8 ± 0.5 atom % Cs, 53.2 ± 0.3 atom % K, and 9.0 ± 0.1 atom % Na. During the sampling, the reaction mixture stood for 25 minutes with no stirring. The flask's green colored contents were then slowly jetted into 500 ml of ice water. After standard workup and gc analysis on a FFAP column (VI, 70°C) the following monomeric products (mmol; mole % yield based on toluene as limiting reagent; retention time) were observed: 2,5-dihydrotoluene (3.21 mmol; 21.6 mole %; 13.3 min.) and toluene (4.60 mmol; 31.2 mole %; 16 min.). On the same basis, analysis by gc on a Carbowax 20-M column (IV, 120°C) gave the following dimeric products: 3,3'-dimethyl-1,1'-4,4'-tetrahydrobiphenyl (3.36 mmol; 45.4 mole %; 13 min.) and an isomeric mixture of 3,3'-dimethyl-1,1',4,6'-tetrahydrobiphenyl and 3,3'-dimethyl-1,1',2,4'-tetrahydrobiphenyl (0.13 mmol; 1.8 mole %; 13.7 min.).

The sample was reduced to an oil on the rotating evaporator. Next 0.200 g of this oil was oxidized overnight by 0.873 g of DDQ in 30 ml of refluxing benzene. The excess DDQ was consumed by the addition of 3 ml of 1,4-dihydrobenzene. The mixture was filtered. By gc analysis on a Carbowax 20-M column (IV, 150°C), the following products (mmol product; mole % yield based on dimer as limiting reagent; gc retention time) were observed: o,o'-dimethylbiphenyl (0.007 mmol; 0.2 mole %; 6.5 min.), o,m'-dimethylbiphenyl (0.024 mmol; 0.7 mole %; 9.9 min., and m,m'-dimethylbiphenyl (3.460 mmol; 99.1 mole %; 19.0 min.).

Synthesis of o,m'-Dimethylbiphenyl

In a standard reaction apparatus, 4.9150 g (202.2 mg-atoms) of

magnesium was slowly stirred in 50 ml of diethyl ether. To this mixture 40.9643 g (187.9 mmol) of m-iodotoluene was added dropwise over a 50 min. period. Due to the exothermic nature of this reaction the ether began to reflux after ten minutes and continued until the addition was complete. Next, 18.0470 g (160.9 mmol) of 2-methyl-cyclohexanone in 100 ml of diethyl ether was added dropwise to the brown Grignard reagent over a 25 minute period. Since this was also an exothermic reaction, the diethyl ether refluxed. After addition of the ketone, the mixture was heated for 15 minutes and then siphoned into 250 ml of 10 % HCl. After standard workup and solvent removal on a rotating evaporator, the alcohol was dissolved in 150 ml of dry benzene in a round bottom flask equipped with a Dean-Stark apparatus. To this solution was added 0.519 g of p-toluenesulfonic acid. The solution was heated at reflux for three hours to dehydrate the alcohol to the alkene. The reaction mixture was extracted with aqueous base to remove the acid. Thus 23.2653 g of crude dehydrated product was isolated. This material (5.158 g) was oxidized overnight with excess DDQ (15.031 g) in 100 ml of refluxing benzene. The excess DDQ was consumed by the addition of 3 ml of 1,4-dihydrobenzene. The mixture was then filtered and the filtrate concentrated on the rotating evaporator. The oil was vacuum distilled in a Hickman apparatus at 60°C and 0.3 mm of Hg. Thus 1.7943 g of gc pure o,m'-dimethylbiphenyl[60] was isolated (overall yield 24.4 %). the ^{1}H NMR (CCl_4) had absorbance at δ 2.20 (3.0 H, s, o-methyl), 2.33 δ (3.0 H, s, m-methyl), and 7.08 (7.9 H, m, aromatic).

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[60]Beilstein, Band 5, 2nd Supplement, p. 512.

Reaction of t-Butylbenzene with Cs-K-Na Alloy

In reaction IV-79, premade Cs-K-Na alloy (44.8 mg-atoms Cs, 44.8 mg-atoms K, 4.8 mg-atoms Na) in a blue THF (350 ml) solution was cooled to -40°C with vigorous stirring. At this temperature, 2.0786 g (15.49 mmol) of t-butylbenzene was syringed into the flask with no change in color. After ten hours, the flask color was still blue and gc analysis of a protonated sample on a Carbowax 20-M column (IV, 60°) showed that no reaction had occurred. The flask temperature was then raised, in the following order, to -33°C for 14 hours, -25°C for one hour, and 0°C for two hours with no reaction occurring according to gc analysis. The flask temperature was then raised to 27°C; after 12 hours the flask color finally became black and gc analysis indicated a 9 rel. area % yield of 2,5-dihydro-t-butylbenzene. (Note that in samples that were either centrifuged to remove solids or had mercury added before protonation no reduction product was observed.) In an attempt to increase the extent of reaction, the flask temperature was raised to 67°C and maintained for seven hours. At this time, the flask's contents were jetted into 500 ml of ice water and a 2 ml gc sample was quenched with I_2.

After standard workup and gc analysis on a Carbowax 20-M column (IV, 60°C) the following monomeric products (mmol; relative area %; mole % based on t-butylbenzene as limiting reagent; gc retention time) were observed: 2,5-dihydro-t-butylbenzene* (2.03 mmol; 13.8 rel area %; 13.1

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*The assignment of structure as 2,5-dihydro-t-butylbenzene is tentative. Since this compound has a shorter gc retention time than t-butylbenzene, it should by analogy to the benzene and toluene systems be 2,5-dihydro-t-butylbenzene.

mole %; 5.1 min.) and t-butylbenzene (12.69 mmol; 86.2 rel. area %; 81.9 mole %; 9.5 min.). Note that the I_2 quench had 16 rel. area % of 2,5-dihydro-t-butylbenzene and 84 rel. area % of t-butylbenzene. These results indicate that the radical anion was protonated by the solvent at 67°C. Gc analysis on the same column (IV, 170°) indicates that 0.7 mole % of the starting material was converted to dimeric products.

Reaction of p-Xylene with Cs-K-Na Alloy

In reaction IV-121, premade Cs-K-Na alloy (39.4 mg-atoms Cs, 42.9 mg-atoms K, 10.9 mg-atoms Na) in a blue THF (350 ml) solution was cooled to -45°C with vigorous stirring. At this temperature, 1.4549 g (13.71 mmol) of p-xylene was syringed into the flask. Upon addition the flask color darkened. The reaction mixture was stirred at -45°C for nine hours and then at -10°C for 12 hours. Gc analysis of samples removed from the reaction flask and hydrolyzed during this period indicated that no reaction had occurred. Thus, the reaction temperature was raised to 20°C for one hour. At this time, a 5 ml sample was quenched with crushed Dry Ice and the bulk of the contents of the flask were jetted into 500 ml of ice water. After standard workup, gc analysis on a Carbowax 20-M column (IV, 130°) indicated that no organic acids were formed in the sample which was carbonated. Gc analysis on a FFAP column (VI, 70°C) for monomeric products and on a Carbowax 20-M column (IV, 150°C) for dimeric products indicated 0.5 mole % total yield of reduction and dimeric products in the main quench which was protonated.

Reaction of m-Xylene with Cs-K-Na Alloy at -48°C

In reaction IV-123, the unreacted Cs-K-Na alloy left in the

300 ml of dry THF. The Cs-K-Na alloy in the light blue THF solution was vigorously stirred for one hour at room temperature and then cooled to -48°C. At this temperature, 0.6704 g (6.315 mmol) of m-xylene in 5.0 ml of THF was syringed into the flask. The flask color slowly darkened over a one hour period to a black color. Subsequently, the color became increasingly green. Thus, after 3.5 hours the flask color was bright green (yellow precipitate in a blue solution). The reaction mixture was slowly jetted into 500 ml of ice water.

After standard workup and gc analysis on a FFAP column (VI, 70°C) the following monomeric products (mmol; mole % yield based on m-xylene as the limiting reagent; gc retention time) were observed: 2,5-dihydro-m-xylene (1.43 mmol; 22.6 mole %; 10.4 min.) and m-xylene (2.48 mmol; 39.3 mole %; 12.6 min.). On the same basis, analysis by gc on a Carbowax 20-M column (IV, 50° for 9 min. then temperature program at 50°/min. to 150°C) gave 3,3',5,5'-tetramethyl-1,1',4,4'-tetrahydrobiphenyl (1.205 mmol; 38.1 mole %; 17 min.).

Following the gc analysis, the reaction mixture was reduced on the rotating evaporator to 0.9496 g of a brown oil. The material was stored in the refrigerator overnight. The dimer crystallized out of the oil as fine white needles. After filtration and washing with a small amount of pentane, 74.6 mg of fine white needles m.p. 96.9 - 96.5°C were isolated. The ^{1}H NMR ($CDCl_3$) of the needles had absorbance at δ 1.70 (12.0 H, s, methyl), 2.50 (6.0 H, m, allyl), and 5.33 (4.0 H, broad s, vinylic). The UV spectrum (95% EtOH) had absorbance at 2730 Å with ε = 102.6. This indicates, since 1,3-cyclohexadiene at 2600 Å has an

ε = 8000, that some 1.3% of the dimer exists as the conjugated diene. (Note that the absorbance of the conjugated diene impurity in the 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl isolated from the reaction of toluene with Cs-K-Na alloy had absorbance at 2670 Å. If we add 50 Å for the additional methyl group the predicted absorbance is at 2720 Å.)

In reaction IV-131, premade Cs-K-Na alloy (62.9 mg-atoms Cs, 72.7 mg-atoms K, 19.8 mg-atoms Na) in a blue THF (350 ml) solution was cooled to -48°C with vigorous stirring. At this temperature, 2.2650 g (21.34 mmol) of m-xylene in 5.0 ml of THF was syringed into the flask. The color instantly turned black and after one minute dark green. At 30 minutes the flask color was bright green (yellow precipitate in a blue solution). The reaction mixture was vigorously stirred for 3 hours at -48°C and then carefully jetted into 500 ml of ice water.

After standard workup and gc analysis on a Carbowax 20-M column (IV, 100°C) the following products (mmol; mole % yield based on m-xylene as limiting reagent; gc retention time) were observed: 2,5-dihydro-m-xylene (2.86 mmol: 13.4 mole %; 2.4 min.), m-xylene (5.92 mmol; 27.8 mole %; 2.7 min.), and 3,3',5,5'-tetramethyl-1,1',4,4'-tetrahydrobiphenyl (5.85 mmol; 54.8 mole %; 41.9 min.). After the gc analysis, the mixture was reduced on the rotating evaporator to 2.0327 g (90 wt. %) of a brown solid-oil mixture. From this mixture was filtered 1.1994 g (53.0 wt. %) of white powderlike dimer mp. 93.5-94.5°C (mp. 96.0-06.5°C after recrystallization from 95% EtOH).

The ^{1}H NMR ($CDCl_3$) and the UV (95% EtOH) spectra were given in the preceding reaction. The ^{13}C NMR ($CDCl_3$) is shown in Figure 5. The

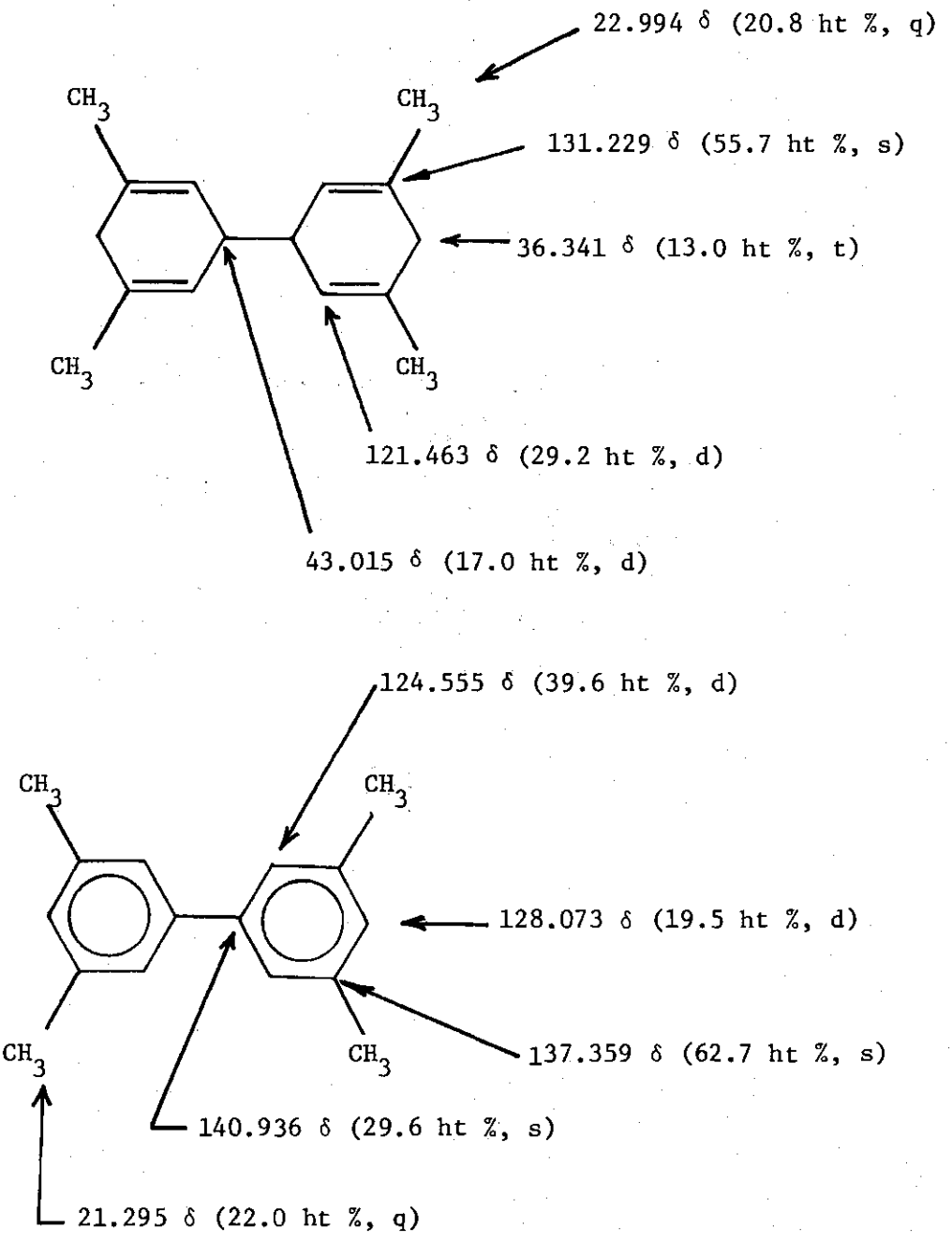

Figure 5. ^{13}C NMR Spectra ($CDCl_3$) of 3,3',5,5'-Tetramethyl-1,1',4,4'-tetrahydrobiphenyl and 3,3',5,5'-Tetramethylbiphenyl with Suggested Assignments for the Absorption Peaks.

low melting dimer placed between two preheated salt plates (100°C) to obtain a thin film for IR spectroscopy. The IR spectrum had absorbance bands at the following wave numbers (cm^{-1}): 3020 (m), 2995 (s), 2960 (s), 2920 (s), 2900 (s), 2860 (s), 2840 (s), 2800 (s), 2780 (s), 2750 (w), 2710 (m), 2640 (w), 2500 (w), 2430 (w), 1860 (w), 1690 (m), 1655 (w), 1595 (w), 1440 (s), 1430 (shoulder), 1385 (s), 1370 (s), 1310 (w), 1275 (m), 1240 (w), 1125 (m), 1090 (w), 1050 (s), 995 (m), 930 (s), 925 (shoulder), 900 (m), 875 (s), 850 (s), 825 (w), 720 (s), and 700 (w). The bands at 3020 (m), 1310 (w), and 850 (s) are evidenced that this compound contains a trisubstituted alkene. The band at 1655 (w) indicates that the double bonds in this compound are unconjugated. Thus the IR spectrum is consistent with the assigned structure of 3,3',5,5'-tetramethyl-1,1',4,4-'-tetrahydrobiphenyl. Mass spectral analysis of the dimer gave the following fragmentation pattern, m/e (relative %): 37 (1), 38 (2), 39 (18), 40 (3), 41 (7), 43 (1), 50 (5), 51 (14), 52 (6), 53 (5), 55 (2), 62 (2), 63 (6), 64 (1), 65 (9), 66 (2), 67 (3), 68 (2), 69 (1), 74 (2), 75 (1), 76 (1), 77 (24), 78 (7), 79 (10), 80 (1), 81 (1), 89 (2), 90 (1), 91 (100), 92 (9), 93 (27), 94 (2), 95 (4), 102 (1), 103 (5), 104 (2), 105 (21), 106 (47), 107 (13), 108 (18), 109 (3), 110 (2), 119 (1), 210 (0.5), 211 (0.25), 212 (0.5), 213 (0.25), 214 (0.5) M^+, 215 (0.25), 216 (1.0) M^+, 217 (0.25), and 218 (0.10). This spectrum indicates that the dimer (M^+ 214) is contaminated with some tetramethyl-hexahydrobiphenyl, M^+ 216. However, the duplicate C, H analysis of the dimer shows the compound to be 89.43% C, 10.49% H and 89.45% C, 10.47% H which closely agrees with the calculated value of 89.65% C and 10.35% H

for a tetramethyltetrahydrobiphenyl. Careful gc analysis of the isolated dimeric material on a Carbowax 20-M column (IV, 130°C), the mass spectral and UV data, and analogy with the benzene and toluene dimeric products gave the following compounds (rel. area %, retention time): 3,3',5,5'-tetramethyl-1,2,3,4,5,6-hexahydrobiphenyl (1.3 rel. area %, 9.0 min.), 3,3',5,5'-tetramethyl-1,1',4,4'-tetrahydrobiphenyl (97.1 rel. area %, 10.6 min.), and 3,3',5,5'-tetramethyl-1,1',2,4'-tetrahydrobiphenyl (1.6 rel. area %, 12.2 min.).

As further confirmation of the dimer structure, 0.206 g of the dimer was oxidized overnight by 0.815 g of DDQ in 50 ml of refluxing benzene. The excess DDQ was consumed by the addition of 3 ml of 1,4-dihydrobenzene. The mixture was filtered and the filtrate concentrated to dryness. This material was then vacuum sublimed (90°C/1 mm Hg). From the sublimation 0.1669 g (82.6 mole % yield) of pure white crystals, m.p. 46-47°C (literature 48.6-49.0°C[61]) were isolated. The ^{1}H NMR (CCl_4) of these crystals has absorbance at δ 2.27 (12.0 H, s, methyl), 6.80 (2.0 H, s, aromatic), and 7.05 (4.0 H, s, aromatic). The ^{13}C NMR is shown in Figure 4. The UV spectrum (95% EtOH) had absorbance at 2550 Å, ε = 15,670 (literature 2550 Å, ε = 16200[62]). The thin film IR spectrum, which was identical to the IR spectrum of 3,3',5,5'-tetramethylbiphenyl found in the literature,[63] had absorbance bands at the following wave

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[61]C. E. Castro, L. T. Andrews, and R. M. Keefer, J. Amer. Chem. Soc., 80, 2322 (1958).

[62]"Ultraviolet Spectral Data." American Petroleum Institute Research Project 44, serial no. 723.

[63]"Infrared Spectral Data." American Petroleum Institute Research Project 44, serial no. 2434.

numbers (cm^{-1}):3750 (w), 3030 (s), 2960 (s), 2920 (s), 2870 (s), 2730 (m), 2380 (w), 2240 (w), 1930 (broad w), 1900 (broad w), 1860 (w), 1840 (w), 1775 (m), 1740 (m), 1730 (m), 1695 (w), 1660 (w), 1630 (s), 1560 (w), 1530 (w), 1475 (s), 1460 (s), 1410 (shoulder), 1385 (m), 1325 (w), 1270 (s), 1200 (w), 1175 (w), 1115 (m), 1050 (s), 1025 (shoulder), 960 (m), 920 (s), 890 (m), 865 (shoulder), 850 (s), 800 (s), 775 (shoulder), 745 (s), and 705 (s). The mass spectrum of the dehydrogenated dimer had the following fragmentation pattern, m/e (relative %): 39 (2), 51 (2), 53 (1), 63 (2), 65 (1), 76 (2), 77 (3), 78 (1), 82 (1), 83 (1), 89 (6), 90 (7), 91 (2), 96 (2), 97 (3), 102 (1), 103 (3), 104 (3), 105 (5), 115 (3), 127 (1), 128 (3), 129 (1), 139 (1), 141 (2), 151 (1), 152 (5), 153 (2), 155 (1), 165 (13), 166 (3), 167 (2), 176 (1), 177 (1), 178 (12), 179 (14), 180 (13), 181 (3), 189 (2), 191 (2), 192 (2), 193 (4), 194 (5), 195 (18), 196 (5), 209 (11), 210 (100) M^+, 211 (18), and 212 (1.8). The duplicate C, H analysis of the compound gave 91.26% C, 8.65% H and 91.31% C, 8.63% H which agree with the calculated composition of 91.37% C and 8.63% H for 3,3',5,5'-tetramethyl-1,1',4,4'-tetrahydrobiphenyl.

The reduction product of m-xylene, 2,5-dihydro-m-xylene (30 mg), was isolated from the reaction mixture by preparative gas chromatography (6' x 1/4" Carbowax column at 80°C). The ^1H NMR spectrum ($CDCl_3$) had absorbance at δ 1.70 (6.0 H, s, methyl), 2.57 (4.0 H, complex m, allyl), and 5.60 (2.0 H, broad s, vinyl). The UV spectrum (95% EtOH) shows essentially no absorbance at 2660 Å (ε = 5.4) which is as expected for an unconjugated diene. The mass spectrum of this compound had the

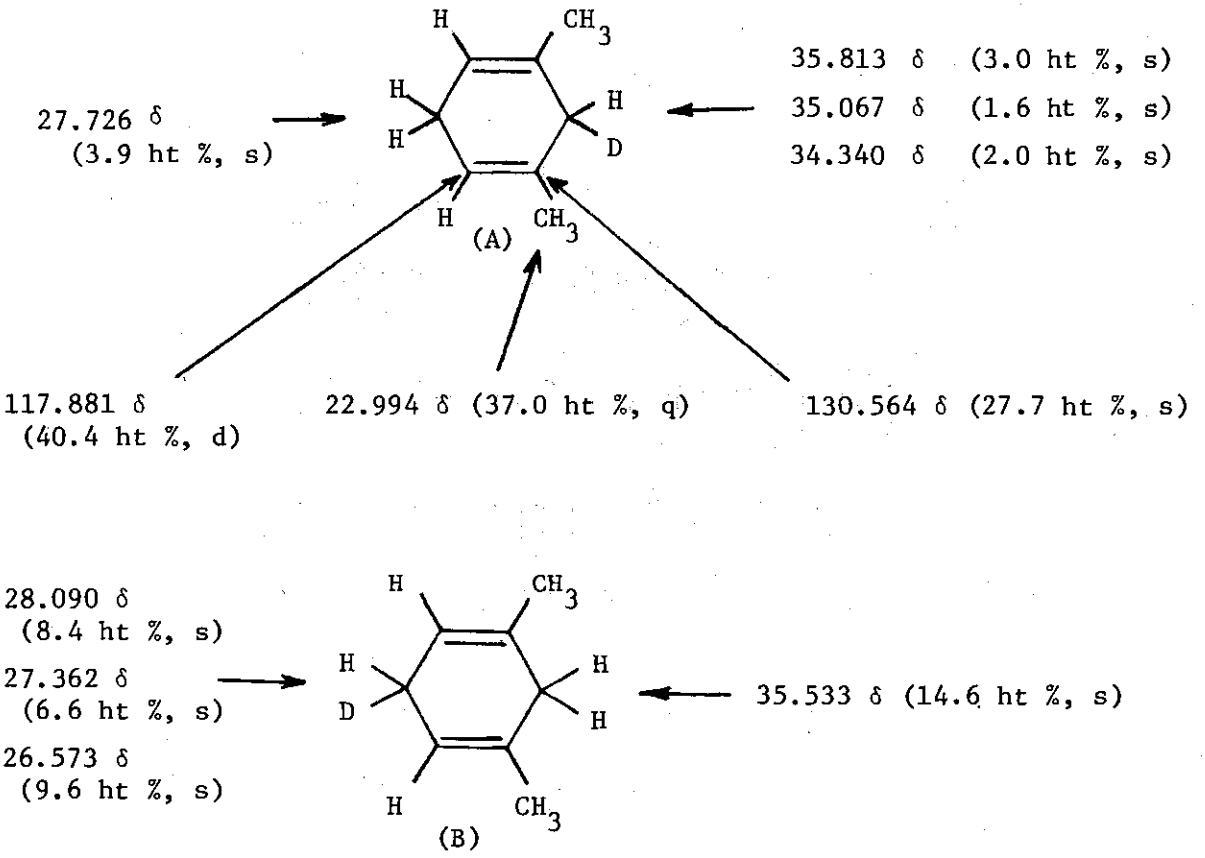
following fragmentation pattern, m/e relative %): 37 (1), 38 (4), 39 (27), 40 (5), 41 (15), 42 (8), 43 (3), 44 (5), 45 (1), 50 (6), 51 (16), 52 (7), 53 (9), 54 (1), 55 (2), 56 (1), 57 (1), 61 (1), 62 (3), 63 (7), 64 (2), 65 (15), 66 (3), 67 (4), 71 (3), 72 (2), 74 (2), 75 (1), 76 (1), 77 (55), 78 (10), 79 (15), 80 (2), 89 (3), 91 (92), 92 (11), 93 (100), 94 (9), 102 (1), 103 (3), 104 (2), 105 (15), 106 (20), 107 (10), 108 (57) M^+, 109 (6), and 110 (0.5).

Reaction of Cs-K-Na Alloy with m-Xylene in the Presence of 18-Crown-6

In reaction IV-147, the premade Cs-K-Na alloy (52.9 mg-atoms Cs 61.3 mg-atoms K, 16.7 mg-atoms Na) in a blue THF (350 ml) solution was cooled to -40°C with vigorous stirring. Once at -40°C, 3.1007 g (11.73 mmol) of crystalline 18-Crown-6 was added to the flask. Upon this addition, the color of the blue solution intensified and the solution viscosity increased. After 30 minutes, 1.2386 g (11.67 mmol) of m-xylene in 5 ml of THF was syringed into the flask. No color change was observed on addition of the m-xylene. The reaction mixture was stirred for three hours at -40°C. The reaction mixture was then jetted into a 250 ml mixture of liquid and solid deuterium oxide (protected from the atmospheric water by a rubber septum). The products were immediately worked-up using standard techniques. By gc analysis on a Carbowax column (IV, 170°C), the following products (mmol; mole % yield based on m-xylene as limiting reagent; gc retention time) were observed: 2,5-dihydro-m-xylene (7.41 mmol; 63.6 mole %; 9 min.) and m-xylene (3.90 mmol; 33.4

mole %; 11.7 min.). Following gc analysis 137 mg of the 2,5-dihydro-m-xylene was isolated by preparative gas chromatography as in the previous reaction. The ^{1}H NMR ($CDCl_3$) had absorbance at δ 1.67 (6.0 H, s, methyl), 2.48 (2.9 H, complex m, allyl), and 5.40 (2.0 H, s, vinyl). Thus, the ^{1}H NMR indicates that this compound is monodeuterated since the allylic region should have 4.0 H if completely protonated. The mass spectrum confirms the ^{1}H NMR evidence of monodeuteration since the major fragmentation peaks were at m/e 78 (47%), 92 (60%), 94 (100%) and 109 (61%) M^+ instead of 77 (55%), 91 (92%), 93 (100%) and 108 (57%) M^+ as in 2,5-dihydro-m-xylene. ^{13}C NMR, which is shown in Figure 6, indicates after careful analysis that the sample is a mixture of 1,5-dimethyl-1,4-cyclohexadiene-6d and 1,5-dimethyl-1,4-cyclohexadiene-3d.

In reaction IV-157, Cs-K-Na alloy (108 mg-atoms Cs, 125 mg-atoms K, 34 mg-atoms Na) in a blue THF (350 ml) solution was cooled to -20°C with vigorous stirring. At this temperature, 12.3826 g (46.85 mmol) of 180crown-6 in 20 ml of THF was added to the flask. Upon addition of the 18-crown-6, the solution color darkened to a dark blue-ink color and all visible signs of the powder-like alloy dispersion were lost. The flask was then cooled to -42°C and 2.5176 g (23.72 mmol) of m-xylene in ten ml of THF was syringed into the flask. There was no color change. The reaction mixture was stirred for four hours at -42°C and then siphoned onto crushed Dry Ice. (Dry Ice was also added to the flask to carbonate residual material.) After standard workup procedures, 3.4560 g of crude acidic material was isolated. Quantitative gc analysis on a SE-30 column (V, 130°C) of the methyl esters of the acidic products (mmol, mole %



$$\frac{(A)}{(B)} = \frac{3.9}{14.6} = \frac{6.6}{24.6} = \frac{1}{3.74}$$

Figure 6. ^{13}CNMR Spectra ($CDCl_3$) of a Mixture of 1,5-Dimethyl-1,4-cyclohexadiene-6d (A) and 1,5-Dimethyl-1,4-cyclohexadiene-3d (B) with Suggested Assignments of the Absorption Peaks.

yield based on m-xylene as limiting reagent, gc retention time) gave the following products: unknown acid (0.32 mmol,* 1.4 mole %, 1.9 min.), 2,6-dimethylbenzoic acid (3.89 mmol, 16.4 mole %, 2.5 min.), unknown acid (14.93 mmol,* 62.9 mole %, 3.2 min.), and 3,5-dimethylbenzoic acid (0.09 mmol, 0.4 mole %, 4.1 min.). The ^{1}H NMR (CCl_4) spectrum of these acids had absorbance at δ 1.70 (5.8 H, s, vinyl methyl), 2.50 (4.2 H, complex m, allyl and aromatic methyl), 3.52 (1.0, s, proton alpha to a carboxyl group), 5.33 (2.0, broad s, vinyl), 7.08 (0.8 H, broad s, aromatic) and 12.02 (1.2 H, s, CO_2H). Note that the ^{1}H NMR (CCl_4) spectrum of 2,6-dimethylbenzoic acid had absorbance at δ 2.47 (6.0 H, s, methyl), 7.06 (3.0 H, m, aromatic), and 12.20 (1.0 H, s, acid). Thus the ratio of 2,6-dimethylbenzoic acid to dihydrodimethylbenzoic acid based on ^{1}H NMR integration of aromatic and vinyl regions is 1:3.75. This ratio from the gc data (i.e., dimethylbenzoic acids to unknowns) is 1:3.83.

The source of the aromatic acids is dehydrogenation of the reaction products during work-up. A sample of the reaction mixture was allowed to stand overnight on a concentrated KOH solution, reduced to dryness on a rotating evaporator (100°C, 3 hours), acidified with concentrated HCl, extracted with diethyl ether, and then dried over $MgSO_4$. Gc analysis of this sample (i.e., methyl esters) on a SE-30 column (V, 130°C) gave the following products (rel. area %, gc retention time): unknown acid (0.3 rel. area %, 2.0 min.), 2,6-dimethylbenzoic acid (16.3

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*Gc response factors for these unknown acids (i.e., dihydrodimethylbenzoic acids) were assumed to be the same as the dimethylbenzoic acids.

rel. area %, 2.5 min.), unknown acid (53.6 rel. area %, 3.4 min.), and 3,5-dimethylbenzoic acid (29.8 rel. area %, 4.1 min.). This contrasts sharply with the sample composition before repeating the standard acid isolation procedure which was: unknown acid (1.7 rel. area %, 2.0 min.), 2,6-dimethylbenzoic acid (20.2 rel. area %, 2.5 min.), unknown acid (77.6 rel. area %, 3.4 min.), and 3,5-dimethylbenzoic acid (0.5 rel. area %, 4.1 min.).

A 0.149 g sample of the reaction acids was dehydrogenated by heating it overnight at 100°C with 0.243 g of 5% of Pd/C. The dehydrogenated acids were then vacuum sublimed (100°C, 0.3 mm Hg) from the charcoal. The weight of isolated acids was 0.032 g (29.2 wt. % yield). The ^{1}H NMR (CCl_4) spectrum of this material had absorbance at δ 2.38 (6.0 H, s, aromatic methyl), 7.20 (1.0 H, s, aromatic), 7.75 (1.9 H, s, aromatic), and 11.17 (1.0 H, s, acidic). This spectrum indicates that the major dehydrogenation product is 3,5-dimethylbenzoic acid, which has a ^{1}H NMR (CCl_4) spectrum with absorbance at δ 2.37 (6.0 H, s, aromatic methyl), 7.20 (1.0 H, s, aromatic), 7.78 (2.0 H, s, aromatic), and 11.10 (1.0 H, s, acidic). The following products (relative area %, gc retention time) were observed by gc analysis of the methyl esters of these dehydrogenated acids on a SE-30 column (V, 130°C): unknown (1.8 rel. area %, 2.0 min.), 2,6-dimethylbenzoic acid (10.8 rel. area %, 3.0 min.), and 3,5-dimethylbenzoic acid (87.4 rel. area %, 4.3 min.).

Another sample of the reaction acids (0.1054 g) was dehydrogenated by oxidation with DDQ (0.1909 g) in refluxing benzene (25 ml) for three hours. The excess DDQ was consumed by the addition of 2 ml of

1,4-dihydrobenzene. The mixture was filtered and a small amount of the filtrate was separated for gc analysis. The following products (relative area %, gc retention time) were observed by gc analysis of the methyl esters of these dehydrogenated acids on a SE-30 column (V, 130°C): unknown acid (1.5 rel. area %, 2.0 min.), 2.6-dimethylbenzoic acid (14.5 rel. area %, 2.9 min.), unknown acid (13.8 rel. area %, 3.4 min.), and 3,5-dimethylbenzoic acid (70.2 rel. area %, 4.1 min.). The filtrate was then extracted three times with aqueous sodium bicarbonate. The aqueous fraction was acidified with concentrated HCl and extracted with three portions of diethylether. The ether fraction was dried over $MgSO_4$, filtered, and the ether distilled off at atmospheric pressure through a one foot long vigreux column. Thus 0.0607 g (78.3 wt. % yield) of solid acids (mp 159-162°C; 3,5-dimethylbenzoic acid mp 170°C; 2,6-dimethylbenzoic acid mp 125°C) were isolated. After many concentrations of the ^1H NMR solution to eliminate a diethyl ether impurity, the volatile dehydro acids were lost. Thus the following ^1H NMR results should be interreted on a qualitative basis. The ^1H NMR ($CDCl_3$) spectrum of these aromatic acids had absorbance at δ 2.38 (6.0 H, s, aromatic methyl of 3,5-dimethylbenzoic acid), 2.43 (4.0 H, s, aromatic methyl of 2,6-dimethylbenzoic acid, 7.16 (2.0 H, broad s, aromatic protons of 2,6-dimethylbenzoic acid), 7.26 (1.0 H, s, aromatic p-protons of 3,5-dimethylbenzoic acid), 7.78 (2.0 H, s, aromatic o-protons of 3,5-dimethylbenzoic acid), and 10.87 (1.6 H, s, acidic). The ^{13}C NMR ($CDCl_3$) spectrum of this mixture had absorbance at δ 177.458 (6.0 ht %, s, carbonyl C of 2,6-dimethylbenzoic acid), 171.876 (4.8 ht %, s, carbonyl C of

3,5-dimethylbenzoic acid), 137.480 (9.6 ht %, s), 134.869 (6.3 ht %),* 129.528 (5.9 ht %),* 127.285 (12.0 ht %),* 125.710 (5.2 ht %),* 21.300 (3.6 ht %, q, methyl C of 3,5-dimethylbenzoic acid), and 20.992 (3.8 ht %, q, methyl C of 2,6-dimethylbenzoic acid.

Reaction of Biphenyl with Cs-K Alloy at 27°C; Analysis of Cs-K Alloy for the Reacting Alkali Metal

In reaction III-101, analysis of a sample of Cs-K alloy (0.2930 ± 0.0002 g Cs-K; 2.964 ± 0.001 mmol MOH) gave an alloy composition of 63.7 ± 0.1 atom % Cs and 36.3 ± 0.1 atom % K. The Cs-K alloy (42.13 mg-atom Cs; 23.93 mg-atom K) in a blue THF (350 ml) solution was vigorously stirred at 27°C for 20 minutes. Then 1.4156 g (9.18 mmol) of biphenyl in 10 ml of THF was syringed into the flask. There was an immediate color change from blue to green to finally black. After 133 minutes, a second alloy sample (0.8883 ± 0.0002 g Cs-K; 9.979 ± 0.001 mmol MOH) was found to have the composition 53.2 ± 0.1 atom % Cs and 46.8 ± 0.1 atom % K. Twenty-five minutes later the reaction mixture was slowly jetted into 500 ml of ice water. After standard work-up and gc analysis on a Carbowax 20-M column (IV, 130°C) the following products (mmol, mole % based on biphenyl as limiting reagent, gc retention time) were observed: phenylcyclohexane (0.04 mmol, 0.4 mole %, 8.6 min.), 3-phenylcyclohexene[64] (0.71 mmol, 8.2 mole %, 10.1 min.), 1,4-dihydrobiphenyl

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*The off resonance multiplicity of these peaks is unintelligible since they extensively overlap each other.

[64]Reference 4, p. 112. These compounds were assumed to have the same molar response value as dicyclohexyl, phenylcyclohexane, 1-phenylcyclohexene, 1,4-dihydrobiphenyl, and biphenyl.

(4.61 mmol, 52.8 mole %, 14.3 min.), 1-phenylcyclohexene (0.39 mmol, 4.5 mole %, 17.7 min.), 3,4-dihydrobiphenyl[64] (0.59 mmol, 6.7 mole % 22.3 min.), and biphenyl (1.98 mmol, 22.6 mole %, 31.8 min.). On the same basis, gc analysis on a FFAP column (VI, 70°C) gave the following cleavage products: cyclohexene (0.25 mmol, 1.4 mole %, 3.9 min.) and benzene (0.58 mmol, 3.2 mole %, 7.5 min.).

In reaction III-115, analysis of a sample of the Cs-K alloy (0.3894 ± 0.0002 g of Cs-K; 4.098 ± 0.010 mmol MOH) gave an alloy composition of 59.6 ± 0.1 atom % Cs and 40.4 ± 0.1 atom % K before the addition of biphenyl. The Cs-K alloy (46.53 mg-atom Cs; 31.52 mg-atom K) in a blue THF (350 ml) solution was vigorously stirred for 20 minutes at 27°C. At this temperature, 1.0846 g (7.03 mmol) of biphenyl in ten ml of THF was syringed into the flask. The reaction mixture color rapidly turned green and then brown-black. After two hours, a second alloy sample (0.6492 ± 0.0002 g of Cs-K; 7.258 ± 0.010 mmol MOH) was analyzed and found to have a composition of 53.7 ± 0.1 atom % Cs and 46.3 ± 0.1 atom % K. Fifteen minutes later, the reaction mixture was carefully siphoned into 300 ml of ice water. After standard work-up and gc analysis on a Carbowax 20-M column (IV, 130°) the following products (mmol, mole % yield based on biphenyl as limiting reagent, gc retention time) were observed: phenylcyclohexane (0.05 mmol, 0.7 mole %, 8.0 min.), 3-phenylcyclohexene[64] (0.48 mmol, 6.8 mole %, 9.6 min.), 1,4-dihydrobiphenyl (3.84 mmol, 54.6 mole %, 12.7 min.), 1-phenylcyclohexene (0.21 mmol, 3.0 mole %, 15.8 min.), 3,4-dihydrobiphenyl[64] (0.56 mmol, 8.0 mole %, 19.5 min.), and biphenyl (1.15 mmol, 16.4 mole %, 27.3 min.). On the same

basis, gc analysis for cleavage products on a FFAP column (VII, 50°C) gave benzene (0.20 mmol, 1.4 mole %, 8.2 min.). (Note, the highly reduced residual material which was extracted from the flask walls accounted for 2.8 mole % of total products, including those biphenyl derivatives identified in the main quench, seven unidentified highly reduced compounds,[64] and dicyclohexyl, see reaction IV-19.)

In reaction IV-19, analysis of a sample of Cs-K alloy (0.8119 ± 0.0002 g of Cs-K; 3.477 ± 0.010 mmol of MOH) gave an alloy composition of 77.4 ± 0.1 atom % Cs and 22.6 ± 0.1 atom % K before the addition of biphenyl. The Cs-K alloy (55.12 mg-atom Cs; 16.08 mg-atom K) in a blue THF (250 ml) solution was stirred vigorously for 30 minutes at 24°C. At this temperature, 2.7634 g (17.92 mmol) of biphenyl in 10 ml of THF was syringed into the flask. The flask color changed immediately from blue to green and then to black. The reaction mixture was stirred for six hours at 24°C. At this time, analysis of a second sample of Cs-K alloy (0.3049 ± 0.0002 g of Cs-K; 3.477 ± 0.010 mmol MOH) gave an alloy composition of 51.8 ± 0.2 atom % Cs and 48.2 ± 0.3 atom % K. After the sampling of the alloy, the flask was allowed to stand for one hour. Thus at seven and one half hours after addition of the biphenyl the flask's contents which had not settled out were carefully jetted into 500 ml of ice water. After standard work-up and gc analysis on a Carbowax 20-M column (IV, 130°C) the following products (mmol, mole % yield based on biphenyl as the limiting reagent, gc retention time) were observed: 3-phenylcyclohexene[64] (0.97 mmol, 5.4 mole %, 7.8 min.), 1,4-dihydrobiphenyl (6.41 mmol; 35.8 mole %, 10.7 min.), 1-phenylcyclohexene (0.59 mmol, 3.3 mole %, 13.2 min.), 3,4-dihydrobiphenyl[64] (0.56 mmol, 3.1 mole

%, 16.3 min.), and biphenyl (2.69 mmol), 15.0 mole %, 22.5 min.). No phenylcyclohexane was observed. Analysis on a FFAP column (VI, 70°C) indicated that no cleavage of biphenyl to benzene derivatives occurred under these mild quenching conditions. Thus the objective of eliminating overreduction during the quench was achieved in this reaction by allowing the alloy to completely settle out of the reaction mixture and then using a 12 gauge stainless steel canula to jet the reaction mixture into the ice water. On the same basis, gc analysis of the highly reduced material which was washed out of the reaction flask accounted for 29.0 mole % of biphenyl derivatives and 2.7 mole % of benzene derivatives. Thus the flask rinse contained the following biphenyl derivatives: unknown[64] (0.17 mmol, 1.0 mole %, 3.7 min.), unknown[64] (0.07 mmol, 0.4 mole %, 4.4 min.), unknown[64] (0.06 mmol, 0.3 mole %, 4.9 min.), unknown[64] (0.06 mmol, 0.3 mole %, 5.4 min.), unknown[64] (0.19 mmol, 1.1 mole %, 6.1 min.), unknown[64] (0.25 mmol, 1.4 mole %, 6.9 min.), phenylcyclohexane (0.22 mmol, 1.2 mole %, 7.3 min.), 3-phenylcyclohexene[64] (0.82 mmol, 4.6 mole %, 8.0 min.), unknown[64] (0.27 mmol, 1.5 mole %, 9.2 min.), 1,4-dihydrobiphenyl (0.31 mmol, 1.7 mole %, 11.0 min.), 1-phenylcyclohexene (0.53 mmol, 2.9 mole %, 13.6 min.), 3,4-dihydrobiphenyl[64] (0.36 mmol, 2.0 mole %, 16.8 min.), and biphenyl (1.30 mmol, 7.3 mole %, 23.2 min.). The flask rinse also contained the following cleavage products: cyclohexene (0.74 mmol, 2.1 mole %, 4.1 min.) and benzene (0.21 mmol, 0.6 mole %, 10.7 min.).

Reaction of Diphenylmethane with Cs-K-Na Alloy at -75°C

In reaction IV-135, Cs-K-Na alloy (27.15 mg-atoms Cs; 31.43 mg-atom K; 8.56 mg-atoms Na) in a blue THF (250 ml) solution was cooled to -75°C with vigorous stirring. At this temperature, 1.2713 g (7.56 mmol)

of diphenylmethane in 5 ml of THF was syringed into the reaction flask. The solution color changed from blue to black after one minute. After two hours at -75°C, the solution color was dark green (blue solution and a yellow precipitate). At this the reaction mixture was carefully jetted into 300 ml of ice water. After standard work-up and gc analysis on a Carbowax 20-M column (IV, 160°C) the following products (mmol, mole % yield based on diphenylmethane as limiting reagent, and gc retention time) were observed: $C_{13}H_{16}$ (0.05 mmol, 0.7 mole %, 4.7 min.), $C_{13}H_{16}$ (0.14 mmol, 1.8 mole %, 6.1 min.), 2,5-dihydrodiphenylmethane (1.89 mmol, 24.9 mole %, 7.3 min.), and diphenylmethane (5.12 mmol, 67.7 mole %, 8.9 min.). The sample was then concentrated by distilling off the diethyl ether through a one foot vigreux column giving a crude yield of 1.2317 g of a brown oil. Part of this oil (0.2175 g) was oxidized overnight by excees DDQ (1.4046 g) in refluxing benzene. The excess DDQ was consumed by the addition of 3 ml of 1,4-dihydrobenzene. The mixture was filtered and the filtrate was concentrated by stripping the benzene off through the one foot vigreux column. Gc analysis on the Carbowax 20-M column (IV, 160°C) showed only diphenylmethane (8.9 min.) and no flourene in this dehydrogenated sample. The ^1H NMR (CCl_4) spectrum of the dehydrogenated product was identical to that of diphenylmethane and has absorbance at δ 3.83 (2.0 H, s, methylene) and 7.02 (10.3 H, s, aromatic).

Reaction of 2,2-Diphenylpropane with Cs-K Alloy at -25°C; Analysis of the Alloy for the Reacting Alkali Metal

In reaction II-91, analysis of a sample of Cs-K alloy (0.3718 ±

0.0002 g of Cs-K, 4.156 ± 0.010 mmol of MOH) gave an alloy composition of 53.6 ± 0.1 atom % Cs and 46.4 ± 0.1 atom % K before the addition of the 2,2-diphenylpropane. The Cs-K alloy (37.14 mg-atom Cs; 32.12 mg-atoms K) in the blue THF (250 ml) solution was cooled to -34°C. At this temperature, 1.5873 g (8.09 mmol) of 2,2-diphenylpropane in 10 ml of THF was syringed into the flask. The flask color instantly turned red. The reaction mixture was stirred for three hours at -25°C. At this time a second Cs-K alloy sample (0.1964 ± 0.0002 g of Cs-K, 2.530 ± 0.010 mmol of MOH) was analyzed and found to have the composition 41.1 ± 0.1 atom % Cs and 58.9 ± 0.1 atom % K. The now brown-black colored reaction mixture was then rapidly siphoned into 250 ml of ice water. After standard work-up and gc analysis on a Carbowax 20-M column (III, 180°C) the following products[65] (mmol, mmol yield based on 2,2-diphenylpropane as limiting reagent, gc retention time) were observed: tetrahydro-2,2-diphenylpropane (0.27 mmol, 3.3 mole %, 6.8 min.), tetrahydro-2,2-diphenylpropane (0.05 mmol, 0.6 mole %, 7.6 min.), and 2,2-diphenylpropane and/or cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene (1.92 mmol, 23.7 mole %, 11.0 min.). On the same basis, gc analysis on a SE-30 column (V, 160°C) gave the following products: tetrahydro-2,2-diphenylpropane and/or 2,2-diphenylpropane (0.60 mmol, 7.4 mole %, 5.6 min.), tetrahydro-2,2-diphenylpropane (0.10 mmol, 1.2 mole %, 6.3 min.), and cis-9,9-dimethyl-4a,4b,2,7-tetrahydroflourene (1.90 mmol, 23.5 mole %, 7.2 min.). Thus the yields of products are quite low with only 23.5 mole % of cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene and 8.6 mole %

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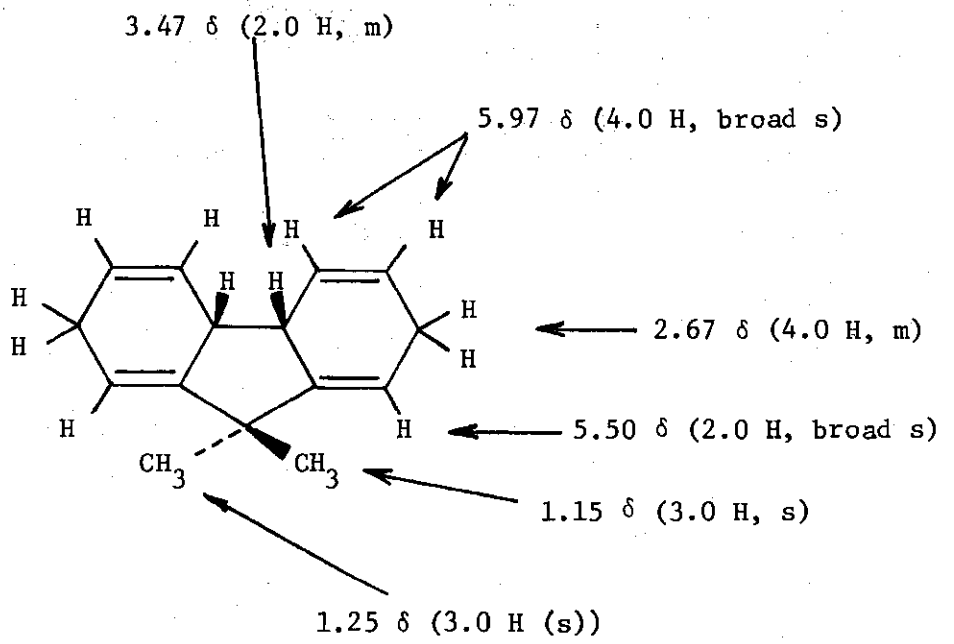
[65]Reference 4, p. 129.

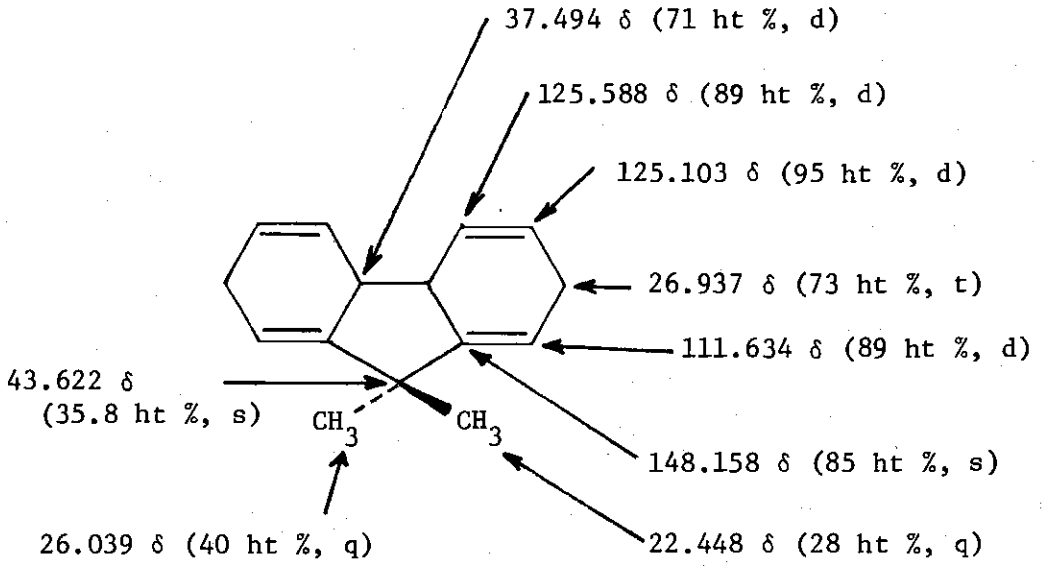
of 2,2-diphenylpropane and its tetrahydro reduction products. Later gc analysis of the reaction mixture on a FFAP column (VI, 70°C) indicated the presence of two cleavage products. The first has the gc retention time of 1,3-cyclohexadiene and the other is presumably a reduced cumene derivative. The yields of these compounds could not be determined since the reaction mixture had been concentrated on the rotating evaporator.

Reaction of 2,2-diphenylpropane with Cs-K-Na Alloy at -75°C

In reaction IV-143, Cs-K-Na alloy (23.31 mg-atoms Cs; 26.99 mg-atoms K; 7.35 mg-atoms Na) in a blue THF (250 ml) solution was cooled to -75°C with vigorous stirring. At this temperature, 0.6108 g (3.11 mmol) of 2,2-diphenylpropane in 5 ml of THF was syringed into the flask. There was an immediate color change from blue to green. After three hours, the reaction mixture was carefully jetted into 500 ml of ice water. After standard work-up and gc analysis on a SE-30 column (V, 140°C), the following products (mmol, mole % yield based on 2,2-diphenylpropane as the limiting reagent, gc retention time) were observed: 2,2-diphenylpropane (0.26 mmol, 8.3 mole %, 7.0 min.) and cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene (2.80 mmol, 89.9 mole %, 9.1 min.). The reaction mixture was then concentrated on the rotating evaporator. The crude product was recrystallized from 95% EtOH to give 0.2379 g of fine white crystals, mp 74-75°C. A second batch from the recrystallization yielded 0.0606 g of fine white crystals, mp 74-75°C. Thus the isolated yield of pure cis-9,9-dimethyl-4a,4b,2,7-tetrahydrofluorene was 0.2985 g or 48.9 wt. %. The ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) of this compound are shown in Figure 7.



(A)



(B)

Figure 7. The ^{1}H NMR ($CDCl_3$) (A) and $^{13}CNMR$ ($CDCl_3$) (B) of cis-9,9-Dimethyl-4a,4b,2,7-tetrahydrofluorene with Suggested Assignments of the Absorption Peaks.

Reaction of 1,1,1-Triphenylethane with Cs-K-Na Alloy at -50°C; Analysis of the Alloy to Determine the Reacting Alkali Metal

In reaction IV-41, analysis of a sample of the Cs-K-Na alloy (0.3037 ± 0.0002 g of Cs-K-Na; 3.668 ± 0.010 mmol of MOH: 1.4113 ± 0.0020 g of Cs-KTPB) gave an alloy composition of 47.4 ± 0.4 atom % Cs, 47.5 ± 0.4 atom % K, and 5.1 ± 0.1 atom % Na before the addition of 1,1,1-triphenylethane. The Cs-K-Na alloy (33.97 mg-atoms Cs; 34.02 mg-atoms K; 3.63 mg-atoms Na) in the blue THF (350 ml) solution was cooled to -50°C with vigorous stirring. At this temperature, 0.8773 g (3.40 mmol) of 1,1,1-triphenylethane in 10 ml of THF was syringed into the reaction flask. Upon addition the reaction flask's deep blue solution darkened, after three minutes, the flask color was dark red. After 70 min., analysis of a second alloy sample (0.2174 ± 0.0002 g of Cs-K-Na; 2.778 ± 0.010 mmol of MOH; 1.0345 ± 0.0020 g of Cs-KTPB) gave an alloy composition of 43.0 ± 0.4 atom % Cs, 49.7 ± 0.5 atom % K, and 7.3 ± 0.1 atom % Na. After sampling the alloy the reaction mixture was carefully jetted into 500 ml of ice water. After standard work-up and gc analysis on a SE-30 column (X, 175°C) the following products[6] (mmol, mole % yield based on 1,1,1-triphenylethane as the limiting reagent, gc retention time) were observed: 1,1,1-triphenylethane (0.49 mmol, 14.4 mole %, 9.4 min.) and cis-9-methyl-9-phenyl-4a,4b,2,7-tetrahydrofluorene (2.27 mmol, 66.9 mole %, 12.9 min.).

In reaction IV-55, analysis of a sample of Cs-K-Na alloy (0.2217 ± 0.0002 g of Cs-K-Na; 2.695 ± 0.010 mmol of MOH; 1.0525 ± 0.0020 g of Cs-KTPB) gave an alloy composition of 46.6 ± 0.4 atom % Cs, 50.2 ± 0.4 atom % K, and 3.2 ± 0.1 atom % Na before the addition of

1,1,1-triphenylethane. The Cs-K-Na alloy (39.88 mg-atoms Cs; 43.03 mg-atoms K; 2.64 mg-atoms Na) in the blue THF (350 ml) solution was cooled to -51°C with vigorous stirring. At this temperature, 0.8925 g (3.45 mmol) of 1,1,1-triphenylethane in 10 ml of THF was syringed into the flask. The flask color changed from blue to red. After 120 min. the stirring was discontinued. At 200 min., a second alloy sample (0.1569 ± 0.0002 g of Cs-K-Na; 2.054 ± 0.010 mmol of MOH: 0.7784 ± 0.0020 g of Cs-K-TPB) was analyzed and found to have a composition 40.1 ± 0.4 atom % Cs, 56.5 ± 0.5 atom % K, and 3.4 ± 0.1 atom % Na. After sampling the alloy, the reaction mixture was stirred up and carefully jetted into 500 ml of ice water. (Note that after 80 minutes with no stirring that the red precipitate had settled out of the blue THF solution.) After standard work-up and gc analysis on a SE-30 column (V, 175°C) the following products (mmol, mole % based on 1,1,1-triphenylethane as the limiting reagent, gc retention time) were observed: 1,1,1-triphenylethane (0.04 mmol, 1.3 mole %, 11.3 min.) and cis-9-methyl-9-phenyl-4a,4b,2,7-tetrahydrofluorene (2.48 mmol), 71.7 mole %, 14.6 min.).

Reaction of Bibenzyl with Cs-K-Na Alloy at -75°C

In reaction IV-83, Cs-K-Na alloy (37.23 mg-atoms Cs; 37.28 mg-atoms K; 3.96 mg-atoms Na) in the blue THF (350 ml) solution was cooled to -75°C with vigorous stirring. At this temperature, 1.0554 g (5.79 mmol) if bibenzyl in 5 ml of THF was syringed into the flask. Upon addition the flask color turned black but after five minutes the flask color was green. The reaction mixture was stirred for 90 minutes at

-75°C and then carefully jetted into 500 ml of ice water. After standard work-up and gc analysis on a FFAP column (VI, 80°C) only the following product (mmol, mole % yield based on bibenzyl as limiting reagent,* gc retention time) was observed: toluene (11.01 mmol, 95.1 mole %, 10.4 min.). Thus it appears that once the dicesium adduct of bibenzyl is formed it readily cleaves giving two equivalents of benzyl cesium, which upon protonation gives toluene.

In reaction IV-93, Cs-K-Na alloy (87.07 mg-atoms Cs; 94.78 mg-atoms K; 24.16 mg-atoms Na) in the blue THF (350 ml) solution was cooled to -75°C with vigorous stirring. At this temperature 2.5468 g (14.04 mmol) of bibenzyl in 10 ml of THF was syringed into the flask. Upon addition the flask color turned black but after five minutes the color was red. The reaction mixture was stirred for one hour at -75°C, and the now bright orange-red reaction mixture was siphoned onto crushed dry ice. The material remaining in the reaction flask was protonated. After standard work-up and gc analysis on a Carbowax 20-M column (IV, 120°C) the following acidic product (mmol, mole % yield based on bibenzyl as the limiting reagent, gc retention time) was observed (as the methyl ester); phenylacetic acid (17.35 mmol, 62.1 mole %, 14.0 min.). On the same basis, gc analysis of the neutral fraction on a FFAP column (VI, 60°) gave the following products: 2,5-dihydrotoluene (0.11 mmol, 0.4 mole %, 9.9 min.) and toluene (0.47 mmol, 1.7 mole %, 11.9 min.). The gc analysis of the residual flask material which had been protonated gave the following products:

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*If all of the bibenzyl cleaves into two fragments then the maximum amount of toluene would be 11.58 mmol.

2,5-dihydrotoluene (0.67 mmol, 2.4 mole %, 9.9 min.) and toluene (3.95 mmol, 14.2 mole %, 11.9 min.). Thus the total gc yield of cleavage products was 80.8 mole %. The solvent was removed from the acid by distillation through a one-foot vigreux column. The crude acid was then vacuum sublimed at 100°C and 1.5 mm Hg. This sublimation yielded 1.8058 g (47.5 mole % isolated yield) of a white powder, mp 76.0 - 76.5°C. The mixed melting point of this powder and an authentic sample of phenylacetic acid had a mp of 76.0 - 76.5°C. The ^{1}H NMR (CCl_4) spectrum of this acid, which was identical to that of an authentic sample of phenylacetic acid, had absorbance at δ 3.40 (2.1 H, s, methylene), 6.87 (5.0 H, s, aromatic), and 11.55 (1.0 H, s, acidic). A sample of this acid was melted and sandwiched between two salt plates at 100°C. This was then used to obtain the IR spectrum of the compound. The IR spectrum of this compound, which was identical to that of phenylacetic acid under the same conditions, had absorbance bands at the following wavenumbers (cm^{-1}): 3050 (s, broad 3400-2200), 2050 (w), 1950 (w), 1890 (w), 1860 (w), 1775 (shoulder), 1700 (s, broad), 1600 (m), 1540 (w), 1495 (m), 1455 (m), 1410 (s), 1335 (w), 1325 (w), 1290 (s), 1240 (m), 1190 (m), 1140 (w), 1100 (w), 1070 (m), 1025 (m), 1010 (s, broad), 835 (m), 750 (s), 700 (s), and 775 (s).

In reaction IV-101, Cs-K-Na alloy (91.05 mg-atoms Cs; 99.11 mg-atoms K; 25.27 mg-atoms Na) in a blue THF (250 ml) solution was cooled to -75°C with vigorous stirring. At this temperature, 2.7168 g (14.905 mmol) of bibenzyl in ten ml of THF was syringed into the flask. Upon addition, the flask color changed from blue to red. The solution color

intensified until the red color appeared almost black. The reaction temperature was maintained at -75°C for 80 minutes. Then the reaction mixture was siphoned onto crushed Dry Ice. (Dry Ice was also added to the flask to carbonate any residual material which had not been removed by the siphoning. After ten minutes, 100 ml of 95% EtOH was added to both the carbonation and reaction flasks.) After standard work-up, this reaction yielded 3.9793 g (98 wt. % yield) of crude acid. By gc analysis on a Carbowax 20-M column (IV, 170°C) the methyl ester of the following acidic product (mmol, mole % yield based on bibenzyl as the limiting reagent, gc retention time) was observed: phenylacetic acid (27.84 mmol, 93.4 mole %, 12.8 min.). On the same basis, gc analysis on a FFAP column (VI, 75°C) gave the following neutral product: toluene (1.30 mmol, 4.4 mole %, 11.5 min.).

Reaction of 1,2-Di-p-tolylethane with Cs-K-Na Alloy

In reaction IV-125, Cs-K-Na alloy (49.12 mg-atoms Cs; 53.47 mg-atoms Cs; 53.47 mg-atoms K; 16.63 mg-atoms Na) in a blue THF (250 ml) solution was cooled to -75°C with vigorous stirring. At this temperature, 0.8316 g (3.95 mmol) of 1,2-di-p-tolylethane in 5 ml of THF was syringed into the flask. Upon addition, the solution color changed from blue to green. The reaction was stirred for 2.5 hours at -75°C. Then the flask was allowed to warm such that the temperature was -65°C at 3.0 hours, -45°C at 4.0 hours, -10°C at 4.5 hours, and 12°C at 5 hours after addition of the hydrocarbon. The green flask color changed at -10°C to a red color. Thus at five hours of reaction time the red-brown reaction mixture was siphoned onto crushed Dry Ice. (Dry Ice was

also added to carbonate the residual material left in the flask. Ten minutes after the carbonation, 100 ml of 95% EtOH was added to both the carbonation and reaction flasks.) After standard work-up, 1.077 g (91.4 wt. % yield if this is the diacid of the starting hydrocarbon) of crude acid was isolated. By gc analysis on a Carbowax 20-M column (IV, 130°C) the methyl ester of the following volatile acid (mmol, mole % yield based on 1,2-di-p-tolylethane is limiting reagent, gc retention time) was observed: p-methylphenylacetic acid (0.50 mmol, 6.2 mole %, 14.0 min.) There was no p-phenylene diacetic acid in this sample. However gc analysis of this mixture at 189°C gave the methyl esters of the following acids (relative %, gc retention time): unknown (9.0 rel. %, 8.8 min.), unknown (15.5 rel. %, 9.8 min.), and unknown (75.5 rel. %, 11.0 min.). (The neutral materials contained 0.1 mole % of p-xylene and 0.3 mole % of 1,2-di-p-tolylethane.) The ^{1}H NMR (CS_2) spectrum of the crude acid had absorbance at δ 1.76 (0.8 H, s, methyl), 2.00 (0.9 H, s, methyl), 2.20 (0.9 H, s, aromatic methyl), 2.27 (0.9 H, s, aromatic methyl similar to that in p-methylphenylacetic acid), 2.53 (1.4 H, m, allyl and benzyl), 3.47 (0.8 H, s, benzylic proton alpha to a carboxylic acid group), 5.60 (0.6 H, m, vinyl), 6.87 (1.4 H, s, aromatic as in bibenzyl), 7.00 (1.0 H, s, aromatic as in p-methylphenylacetic acid), 7.20 (0.3 H, s, aromatic), and 9.90 (1.0 H, s, CO_2H). Since the ratio of hydrogen in the acidic, aromatic, and vinylic regions is 1.0 H: 2.7 H: 0.6 H and there are four aromatic hydrogens or two vinylic hydrogens per ring, the ratio of acid functions to rings is 1:1. Therefore this mixture consists mainly of diacid derivatives of 1,2-di-p-tolylethane.

The mass spectrum of the methyl esters of the crude acid mixture has the following fragmentation pattern, m/e (relative %): 39 (8), 41 (6), 43 (13), 51 (9), 53 (6), 55 (5), 59 (30), 65 (9), 77 (36), 78 (12), 79 (23), 89 (5), 91 (28), 102 (6), 103 (33), 104 (27), 105 (100), 106 (28), 115 (11), 117 (12), 118 (7), 119 (55), 120 (10), 121 (6), 131 (18), 132 (7), 133 (14), 135 (7), 145 (10), 163 (31), 164 (6), 165 (6), 177 (9), 178 (7), 179 (14), 191 (13), 192 (5), 221 (9), 237 (49), 238 (12), 268 (7), 269 (15), 294 (11), 295 (6), 296 (8), 326 (4), 327 (1), 328 (2) M^+, 329 (0.2), and 330 (0.05). Thus, the ^1H NMR and mass spectral data indicates that these diacid are derived from benzyl and side-chain metalation of 1,2-di-p-tolylethane.

Reaction of 2,3-Dimethyl-2,3-diphenylbutane with Cs-K-Na Alloy at -75°C

In reaction IV-97, Cs-K-Na alloy (87.41 mg-atoms Cs; 95.15 mg-atoms K; 24.26 mg-atoms Na) in a blue THF (350 ml) solution was cooled to -75°C with vigorous stirring. At this temperature, 2.8009 g (11.78 mmol) of 2,3-dimethyl-2,3-diphenylbutane in 10 ml of THF was syringed into the flask. The solution color immediately darkened to a black color and then rapidly turned red. The reaction mixture was vigorously stirred for 155 minutes at -75°C and then was siphoned onto crushed Dry Ice. (Dry Ice was also added to the flask to carbonate any residual material. After ten minutes, 100 ml of 95% EtOH was added to both the carbonation and reaction flasks.) After standard work-up, the isolated yield of crude acid was 3.803 g (98.5 mole %). By gc analysis on a Carbowax 20-M column (IV, 130°C), the methyl ester of the following

acidic product (mmol, mole % yield based on 2,3-dimethyl-2,3-diphenylbutane as the limiting reagent, gc retention time) was observed: α,α-dimethylphenylacetic acid (23.31 mmol, 99.0 mole %, 9.4 min.). On the same basis, gc analysis of the neutral materials on a Carbowax 20-M column (IV, 50°C) gave the following product: cumene (0.17 mmol, 0.7 mole %, 8.0 min.). The crude acid not used in the gc analysis was vacuum sublimed at 90-140°C at 1 mm of Hg. This sublimation yielded 3.6186 g (93.7 mole %) of α,α-dimethylphenylacetic acid, mp 74.0-75.0°C. Recrystallization from hexane resulted in white needles mp 78.0-79.0°C. The mixture melting point of this acid with an authentic sample of α,α-dimethylphenylacetic acid purified in the same manner was 78.0-79.0°C. The ^{1}H NMR (CS_2) spectrum of this acid, which was identical to that of authentic α,α-dimethylphenylacetic acid, had absorbance at δ 1.73 (6.3 H, s, methyl), 7.46 (5.1 H, broad s, aromatic), and 12.56 (1.0 H, s, acidic). A sample of this acid was melted on and then sandwiched between two salt plates at 100°C to obtain a thin film. The IR spectrum of this thin film, which was identical to that of authentic α,α-dimethylphenylacetic acid, had absorbance bands at the following wavenumbers (cm^{-1}): 3000 (s, broad 3400-2200), 2125 (w), 1970 (m), 1885 (m), 1840 (w), 1820 (w), 1780 (w), 1750 (m), 1700 (s, broad), 1610 (m), 1590 (m), 1560 (w), 1540 (w), 1500 (m), 1475 (m), 1450 (s), 1420 (m), 1400 (m), 1375 (s), 1335 (m), 1300 (s, broad), 1240 (m), 1180 (m), 1170 (s), 1105 (m), 1080 (m), 1035 (m), 1005 (w), 990 (w), 975 (m), 940 (s, broad), 905 (m), 840 (m), 775 (m), 765 (m), 730 (m), 700 (s), and 630 (m).

Reaction of 1,2,2-Triphenylpropane with Cs-K-Na at -75°C

In reaction IV-115, Cs-K-Na alloy (43.81 mg-atoms Cs; 47.69 mg-atoms K; 12.16 mg-atoms Na) in a blue THF (350 ml) solution was cooled to -75°C with vigorous stirring. At this temperature, 1.0263 g (3.77 mmol) of 1,2,2-triphenylpropane in 5 ml of THF was syringed into the flask. The color changed from blue to green to yellow-orange. This yellow-orange color intensified until the color was orange-black. After 75 minutes at -75°C, the reaction mixture was siphoned onto crushed Dry Ice. (Dry Ice was then added to the flask to carbonate the remaining residual material. After 15 minutes, 100 ml of 95% EtOH was added to both the reaction and carbonation flasks.) After standard work-up, the isolated yield of crude acids was 0.8738 g. By gc analysis on a SE-30 column (X, 180°C), the methyl esters of the following acidic products (mmol, mole % yield based on 1,2,2-triphenylpropane as the limiting reagent, gc retention time) were observed: phenylacetic acid (3.20 mmol, 84.8 mole %, 1.8 min.) and 2,2-diphenylpropionic acid (3.29 mmol, 87.3 mole %, 7.1 min.). On the same basis, gc analysis of the neutral materials on a FFAP column (VI, 70°C) gave toluene (0.44 mmol, 11.5 mole %, 12.2 min.) and on an OV-17 column (II, 180°C) gave 1,1-diphenylethane (0.31 mmol, 8.2 mole %, 3.35 min.). The ^{1}H NMR (CS_2) spectrum of the acids isolated from this reaction had absorbance at δ 1.82 (3.0 H, s, methyl from 2,2-diphenylpropionic acid), 3.52 (1.5 H, s, benzyl from phenylacetic acid), 7.17 (14.1 H, s, aromatic), and 10.77 (1.5 H, s, acidic). The acid mixture was vigorously shaken in ten ml of hot water to dissolve the phenylacetic acid. The resulting mixture was filtered

and the filtrate was extracted with diethyl ether. The ether was dried over $MgSO_4$, filtered, and placed in an evaporating dish. After evaporation of the ether, 50 mg of white crystalline plates, mp 73-74°C, were removed from the dish walls. The mixture melting point of these plates and authentic phenylacetic acid was 73-73°C. The ^1H NMR spectrum (CS_2) of these plates, which was identical to that of authentic phenylacetic acid, had absorbance at δ 3.46 (2.0 H, s, benzylic), 7.07 (4.8 H, s, aromatic), and 10.50 (1.0 H, s, CO_2H). The acids which did not dissolve in the hot water were recrystallized from 50% EtOH. This resulted in a 0.3769 g yield of fine white crystals, mp 166-167°C. The mixture melting point of these crystals and authentic 2,2-diphenylpropionic acid was 166-167°C. The ^1H NMR spectrum (CS_2) of these crystals, which was identical to that of authentic 2,2-diphenylpropionic acid, had absorbance at δ 1.80 (2.9 H, s, methyl), 7.10 (10.0 H, s, aromatic), and 9.90 (1.0 H, s, CO_2H).

Reaction of 1,3-Diphenylpropane with Cs-K-Na Alloy; Analysis of the Alloy to Determine the Reacting Alkali Metal

In reaction IV-5, analysis of a sample of Cs-K-Na alloy (0.4633 ± 0.0002 g of Cs-K-Na; 6.039 ± 0.010 mmol MOH; 2.185 ± 0.0020 g of Cs-KTPB) was found to have a composition 41.8 ± 0.4 atom % Cs, 48.2 ± 0.4 atom % K, and 10.0 ± 0.1 atom % Na before the addition of 1,3-diphenylpropane. The Cs-K-Na alloy (48.49 mg-atoms Cs; 55.90 mg-atoms K; 11.58 mg-atoms Na) in a blue THF (350 ml) solution was cooled to -42°C with vigorous stirring. At this temperature, 1.2907 g (6.58 mmol) of 1,3-diphenylpropane in five ml of THF was syringed into the flask. The flask color changed from blue to green over a five minute period. The flask was

stirred for 21 hours at -42°C. At this time, a second alloy sample (0.5558 ± 0.0002 g Cs-K-Na; 7.912 ± 0.010 mmol MOH; 2.771 ± 0.002 g Cs-KTPB) was withdrawn from the flask and found to have the composition 35.2 ± 0.4 atom % Cs, 53.3 ± 0.4 atom % K, and 11.5 ± 0.1 atom % Na. The reaction mixture was then carefully jetted into 500 ml of ice water. After standard work-up and gc analysis on a Carbowax 20-M column (IV, 170°) the following products (mmol, mole % yield based on 1,3-diphenylpropane as the limiting reagent, gc retention time) were observed: unknown (0.03 mmol, 0.5 mole %, 6.4 min.), 1,3-bis (2',5'-dihydrophenyl)propane (2.09 mmol, 31.8 mole %, 7.2 min.), unknown (0.11 mmol, 1.7 mole %, 8.4 min.), a dihydro-1,3-diphenylpropane (0.39 mmol, 5.0 mole %, 9.2 min.), unknown (0.13 mmol, 2.0 mole %, 10.0 min.), 1-(2',5'-dihydrophenyl)-3-phenylpropane (2.20 mmol, 33.5 mole %, 11.2 min.), 1,3-diphenylpropane (1.02 mmol, 15.5 mole %, 12.5 min.), and a dihydro-1,3-diphenylpropane (0.08 mmol, 1.3 mole %, 16.5 min.). Samples of the major products were isolated by preparative gc and analyzed by mass spectrometry. Thus, the mass spectrum of 1,3-bis(2',5'-dihydrophenyl)propane had the following fragmentation peaks, m/e (rel. %): 39 (6), 40 (2), 41 (10), 42 (3), 43 (6), 44 (8), 50 (2), 51 (4), 52 (3), 53 (4), 54 (2), 55 (6), 56 (2), 57 (4), 65 (6), 66 (2), 67 (8), 68 (2), 69 (3), 77 (8), 78 (7), 79 (10), 80 (11), 81 (12), 82 (2), 83 (2), 84 (2), 91 (14), 92 (16), 93 (6), 94 (4), 95 (20), 96 (8), 103 (2), 104 (100), 105 (26), 106 (6), 107 (2), 108 (3), 109 (3), 111 (2), 141 (2), 149 (2), 200 (12)M^+, 201 (2), and 202 (0.1). The mass spectrum of the dihydro-1,3-diphenylpropane compound of gc retention time 9.2 min. had the following fragmentation peaks, m/e (rel. %): 39 (11), 40 (6),

41 (10), 44 (78), 51 (7), 65 (10), 76 (4), 77 (18), 78 (10), 79 (56), 80 (6), 81 (4), 91 (48), 92 (18), 93 (9), 94 (100), 95 (10), 104 (48), 105 (18), 152 (6), 153 (7), 154 (28), 155 (4), 156 (1), 198 (15) M^+, 199 (2), and 200 (0.2). The mass spectrum of 1-(2',5'-dihydrophenyl)-3-phenylpropane had the following fragmentation peaks, m/e (rel. %): 39 (10), 41 (7), 51 (8), 63 (4), 65 (15), 77 (22), 78 (9), 79 (60), 80 (6), 91 (69), 92 (100), 93 (12), 94 (42), 95 (3), 103 (6), 104 (39), 105 (42), 106 (6), 115 (5), 117 (5), 118 (3), 128 (3), 129 (3), 152 (3), 153 (3), 154 (6), 155 (2), 165 (7), 166 (3), 167 (12), 168 (7), 178 (4), 179 (6), 181 (5), 194 (11), 195 (1), 196 (54), 197 (9), 198 (21) M^+, 199 (3), and 200 (0.5). The mass spectrum of the dihydro-1,3-diphenylpropane of gc retention time 16.5 min. had the following fragmentation peaks, m/e (rel. %): 39 (17), 41 (12), 43 (6), 44 (14), 50 (8), 51 (17), 52 (6), 53 (5), 55 (5), 63 (9), 64 (6), 65 (15), 74 (5), 75 (5), 76 (14), 77 (35), 78 (16), 79 (55), 80 (12), 81 (5), 91 (63), 92 (35), 93 (11), 94 (76), 95 (8), 102 (5), 103 (6), 104 (38), 105 (20), 106 (5), 107 (5), 115 (8), 117 (5), 120 (6), 128 (6), 141 (6), 151 (6), 152 (21), 153 (25), 154 (100), 155 (18), 156 (4), 196 (9), 197 (2), 198 (29) M^+, 197 (5), and 198 (1). Two of the major products were isolated (20 mg each, 90% gc pure) by preparative liquid chromatography of 1 gram of the reaction products on a E. M. Merck Silica Gel 60 prepacked column using pentane as an elutant. The ^1H NMR ($CDCl_3$) spectrum of 1,3-bis(2',5'-dihydrophenyl)propane had absorbance at δ 1.23 (2.0 H, m, aliphatic), 1.60 (7.8 H, m, allylic), 2.53 (3.9 H, broad s, allylic), and 5.57 (6.0 H, m, vinylic). The ^1H NMR ($CDCl_3$) spectrum of 1-(2',5'-dihydrophenyl)-3-

phenylpropane had absorbance at δ 1.23 (1.8 H, m, aliphatic), 1.6 (4.0 H, m, allylic), 2.67 (4.2 H, m, allylic and benzylic), 5.67 (3.0 H, broad s, vinylic), and 7.17 (4.9 H, s, aromatic).

In reaction I-112, analysis of a sample of Cs-K-Na alloy (0.1820 g, dissolved in water) by flame emission spectroscopy at 5890 Å for Na, 4556 Å for Cs, and 4044 Å for K and comparison with the % emission at each wavelength with solutions of the respective alkali metal chloride of known concentration gave an alloy composition of 43.6 atom % Cs, 42.6 atom % K, and 13.8 atom % Na before the addition of 1,3-diphenylpropane. The Cs-K-Na alloy (81.2 mg-atoms Cs; 79.4 mg-atoms K; 25.5 mg-atoms Na) in a blue THF (250 ml) solution was cooled to -75°C with vigorous stirring. At this temperature, 4.0551 g (20.66 mmol) of 1,3-diphenylpropane in five ml of THF was syringed into the flask. The solution color changed from blue to green. The reaction mixture was stirred for one hour at -75°C, for one hour at -60°C, and then one hour at -20°C. At this temperature, a second alloy sample (0.0456 g) was removed from the flask and dissolved in water. Flame emission analysis of this sample gave an alloy composition of 33.9 atom % Cs, 49.8 atom % K, and 16.3 atom % Na. At -20°C, a sample of the reaction mixture was siphoned into a quartz ESR tube. The ESR spectrum of this sample, run at -80°C, had a broad peak with no fine structure at g = 2.1001 (doublet state, no triplet state was observed). The peak intensity, when compared to the peak intensity of a measured sample of 2,2-diphenyl-1-picrylhydrazyl in THF run under identical conditions, gave a radical anion concentration of 5.15×10^{-2} molar. Since the concentration of 1,3-diphenylpropane was 8.16×10^{-5} molar and the concentration of available aromatic

rings was 16.32 x 10^{-5} molar, the yield of radical anion based on the concentration of aromatic rings was 31.5 mole %. A five ml sample of the reaction mixture was then protonated. By gc analysis on a Carbowax 20-M column (I, 190°C), the following products (relative area %, gc retention time) were observed: 1,3-bis(2',5'-dihydrophenyl)propane (34.3 rel. area %, 10.2 min.), a dihydro-1,3-diphenylpropane (7.6 rel. area %, 13.8 min.), 1-(2',5'-dihydrophenyl)-3-phenylpropane (17.3 rel. area %, 15.8 min.), and 1,3-diphenylpropane (40.8 rel. area %, 18.6 min.). Then the bulk of reaction mixture was siphoned into a solution of 183 mg-atoms of iodine in 400 ml of THF. This solution was then extracted with aqueous sodium thiosulfate to remove the iodine. Thus after standard work-up and gc analysis on the Carbowax 20-M column (I, 190°C) only 1,3-diphenylpropane was observed. The sample was concentrated on the rotating evaporator to 4.5995 g of crude 1,3 diphenylpropane. The ^{1}H NMR (CCl_4) spectrum of this sample, which was identical to that of authentic 1,3-diphenylpropane, had absorbance at δ 1.93 (2.3 H, m, aliphatic), 2.63 (3.9 H, t, benzylic), and 7.12 (10.0 H, s, aromatic).

In reaction II-15, analysis of a sample of Cs-K-Na alloy (0.6951 g, dissolved in water) by flame emission spectroscopy gave an alloy composition of 56.6 atom % Cs, 39.8 atom % K, and 3.6 atom % Na before the addition of 1,3-diphenylpropane. The Cs-K-Na alloy (85.64 mg-atoms Cs; 60.22 mg-atoms K; 5.45 mg-atoms Na) in the blue THF (250 ml) was cooled to -75°C with vigorous stirring. At this temperature, 4.0362 g (20.56 mmol) of 1,3 diphenylpropane in 5 ml THF was syringed into the

flask. The solution color changed from blue to green within thirty seconds of the addition. The reaction mixture was stirred for 120 minutes at -75°C, 20 minutes at -60°C, 25 minutes at -50°C, and then 75 minutes at -20°C. At this time a second alloy sample (0.2219 g) was removed from the flask and dissolved in water. Flame emission analysis of this sample gave an alloy composition of 42.9 atom % Cs, 48.0 atom % Na, and 9.1 atom % Na. The reaction mixture was then siphoned into 500 ml of ice water. After standard work-up and gc analysis on a Carbowax 20-M column (I, 190°C), the following products (relative area %, gc retention time) were observed: 1,3-bis(2',5'-dihydrophenyl)propane (37.5 rel. area %, 7.2 min.), unknown (1.3 rel. area %, 8.2 min.), a dihydro-1,3-diphenylpropane (8.9 rel. area %, 8.7 min.), 1-(2',5'-dihydrophenyl)-3-phenylpropane (28.7 rel. area %, 10.3 min.), 1,3-diphenylpropane (21.9 rel. area %, 11.4 min.), and a dihydro-1,3-diphenylpropane (1.7 rel. area %, 14.5 min.).

Reaction of 1,3-Diphenylpropane with Cs-K Alloy; Analysis of the Alloy to Determine the Reacting Alkali Metal

In reaction II-115, analysis of a sample of Cs-K alloy (0.8239 ± 0.0002 g Cs-K; 8.064 ± 0.010 mmol MOH) gave an alloy composition of 67.2 ± 0.5 atom % Cs and 32.8 ± 0.3 atom % K before the addition of 1,3-diphenylpropane. The Cs-K alloy (35.03 mg-atoms Cs; 17.07 mg-atoms K) in the blue THF (250 ml) solution was cooled to -20°C with vigorous stirring. At this temperature, 1.5894 g (8.10 mmol) of 1,3-diphenylpropane in five ml of THF was syringed into the flask. The solution

color immediately changed from blue to green upon addition of the hydrocarbon. After 25 minutes, however, the solution color changed from green to red. After three hours at -20°C, analysis of a second alloy sample (0.2486 ± 0.0002 g Cs-K; 2.838 ± 0.010 mmol MOH) gave an alloy composition of 51.7 ± 0.4 atom % Cs and 48.3 ± 0.4 atom % K. The reaction mixture was then siphoned into 500 ml of ice water. After standard work-up and gc analysis on a Carbowax 20-M column (IV, 170°C), the following products (mmol, mole % yield based on 1,3-diphenylpropane as the limiting reagent, gc retention time) were observed: 1,3-bis(2',5'-dihydrophenyl)propane (1.30 mmol, 16.0 mole %, 11.9 min.), a dihydro-1,3-diphenylpropane (0.58 mmol, 7.2 mole %, 16.6 min.), 1-(2',5'-dihydrophenyl)-3-phenylpropane (1.85 mmol, 22.8 mole %, 20.8 min.), and 1,3-diphenylpropane (1.24 mmol, 15.3 mole %, 23.8 min.).

In reaction III-137, analysis of a sample of Cs-K alloy (0.7936 ± 0.0002 g Cs-K; 7.139 ± 0.010 mmol MOH) gave an alloy composition of 76.8 ± 0.5 atom % Cs and 23.2 ± 0.2 atom % K before the addition of 1,3-diphenylpropane. The Cs-K alloy (54.04 mg-atoms Cs; 16.31 mg-atoms K) in the blue THF (350 ml) solution was cooled to -11°C with vigorous stirring. At this temperature, 3.7161 g (18.93 mmol) of 1,3-diphenylpropane in ten ml of THF was syringed into the flask. The blue solution color disappeared upon the addition of this hydrocarbon. The colorless solution rapidly turned pink and then dark green. After ten minutes, the flask color was red. After three hours, analysis of a second alloy sample (0.6941 ± 0.0002 g Cs-K; 7.720 ± 0.010 mmol MOH) gave an alloy composition of 54.2 ± 0.4 atom % Cs and 45.8 ± 0.4 atom % K. The

reaction mixture was then jetted into 500 ml of ice water. After standard work-up and gc analysis on a Carbowax 20-M column (IV, 140°C), the following products (mmol, mole % yield based on 1,3-diphenylpropane as the limiting reagent, gc retention time) were observed: 1,3-bis(2',5'-dihydrophenyl)propane (0.25 mmol, 1.3 mole %, 7.6 min.), unknown (0.07 mmol, 0.4 mole %, 9.0 min.), a dihydro-1,3-diphenylpropane (2.79 mmol, 14.8 mole %, 9.9 min.), 1-(2',5'-dihydrophenyl)-3-phenylpropane (7.48 mmol, 39.5 mole %, 12.2 min.), 1,3-diphenylpropane (7.19 mmol, 38.0 mole %, 13.5 min.), and a dihydro-1,3-diphenylpropane (0.10 mmol, 0.5 mole %, 17.8 min.).

Reaction of Cyclohexyl Chloride with Cs-K Alloy at 25°C; Analysis of the Alloy for the Reacting Alkali Metal

In reaction III-127, analysis of a sample of Cs-K alloy (0.2484 ± 0.0002 g Cs-K; 2.515 ± 0.010 mmol MOH) gave an alloy composition of 63.6 ± 0.5 atom % Cs and 36.4 ± 0.4 atom % K before the addition of cyclohexyl chloride. The Cs-K alloy (61.11 mg-atoms Cs; 34.94 mg-atoms K) in the blue THF (350 ml) solution was vigorously stirred at 25°C. At this temperature, 3.0787 g (25.96 mmol) of cyclohexyl chloride in ten ml of THF was added dropwise over a seven minute period. Upon addition of the first drop the solution color changed rapidly from blue to pink to colorless. With additional drops of the cyclohexyl chloride solution the flask color turned yellow and then green (yellow precipitate in a blue solution). After five minutes, the flask temperature had risen from 25°C to 30°C. At seven minutes, all of the chloride had been added and the flask temperature was 37°C. At 18 minutes, analysis

of a second alloy sample (1.8900 g ± 0.0020 g Cs-KTPB; 4.892 ± 0.010 mmol MOH) gave an alloy composition of 29.9 ± 0.3 atom % Cs and 70.1 atom % K. At 38 minutes, the reaction mixture was siphoned into 250 ml of ice water. After standard work-up and gc analysis on a FFAP column (VII, 60° for 20 minutes and then temperature pro-ram at 60°/min. to 140°C), the following products (mmol, mole % yield based on cyclohexyl chloride as the limiting reagent, gc retention time) were observed: cyclohexane (22.92 mmol, 88.3 mole %, 2.6 min.), cyclohexene (0.32 mmol, 1.2 mole %, 3.7 min.), and cyclohexyl chloride (0.36 mmol, 1.4 mole %, 22.0 min.).

In reaction IV-33, analysis of a sample of Cs-K alloy (0.2853 ± 0.0002 g Cs-K, 2.617 ± 0.010 mmol (MOH) gave an alloy composition of 74.5 ± 0.4 atom % Cs and 25.5 ± 0.3 atom % K before the addition of cyclohexyl chloride. The Cs-K alloy (52.43 mg-atoms Cs; 17.90 mg-atoms K) in the blue THF (300 ml) solution was vigorously stirred at 25°C. At this temperature, 2.2612 g (19.06 mmol) of cyclohexyl chloride in five ml of THF was syringed into the reaction flask over a 30 second period. Upon addition the blue THF solution became colorless. After 30 seconds, the color was bright yellow; and after an additional 30 seconds, the color was green (yellow precipitate in a blue solution). The reaction mixture was stirred for 16 minutes at 25°C. At this time, analysis of a second sample of the Cs-K alloy (0.2850 ± 0.0002 g Cs-K; 3.028 ± 0.010 mmol MOH) gave an alloy composition of 55.0 ± 0.4 atom % Cs and 45.0 ± 0.4 atom % K. At 45 minutes, the reaction mixture was jetted into 500 ml of ice water. After standard work-up and gc analysis on a FFAP column (VI, 70°C), the following product (mmol, mole % yield

based on cyclohexyl chloride as the limiting reagent, gc retention time) was observed: cyclohexane (18.61 mmol, 97.6 mole %, 2.6 min.).

Reaction of 2,2,3-Triphenylpropyl Chloride with Cs-K-Na Alloy; Analysis of the Alloy for the Reacting Alkali Metal

In reaction IV-105, analysis of a sample of Cs-K-Na alloy (0.4402 ± 0.0002 g Cs-K-Na; 5.526 ± 0.010 mmol MOH; 1.850 ± 0.010 g Cs-KTPB) gave an alloy composition of 47.0 ± 0.4 atom % Cs, 34.1 ± 0.4 atom % K, and 18.9 ± 0.2 atom % Na before the addition of the 2,2,3-triphenylpropyl chloride. The Cs-K-Na alloy (49.06 mg-atoms Cs; 35.56 mg-atoms K; 19.69 mg-atoms Na) in the blue THF (350 ml) solution was cooled to -40°C with vigorous stirring. At this temperature, 1.4659 g (4.78 mmol) of 2,2,3-triphenylpropyl chloride in ten ml of THF was syringed into the reaction flask over a two minute period. The flask color instantly turned from blue to red. After eight minutes, analysis of a second alloy sample (0.1641 ± 0.0002 g Cs-K-Na; 2.156 ± 0.010 mmol MOH; 0.706 ± 0.010 g Cs-KTPB) gave an alloy composition of 42.9 ± 0.4 atom % Cs, 37.3 ± 0.4 atom % K, and 19.8 ± 0.2 atom % Na. The reaction mixture was then siphoned onto crushed Dry Ice. (Dry Ice was also added to the reaction flask to carbonate the remaining residual material. After ten minutes, 100 ml of 95% EtOH was added to both the reaction and carbonation flasks.) After standard work-up and gc analysis on a SE-30 column (X, 210°C), the methyl esters of the following acids (mmol, mole % yield based on 2,2,3-triphenylpropyl chloride as the limiting reagent, gc retention time) were observed: 2,2-diphenylpropionic acid (0.60 mmol, 12.6 mole %, 2.0 min.) and 2-benzyl-2,3-diphenylpropionic

acid (0.53 mmol, 11.1 mole %, 11.7 min.). On the same basis, gc analysis on this column (X, 180°C) gave the methyl ester of phenylacetic acid (2.86 mmol, 59.9 mole %, 1.8 min.). On the same basis, gc analysis on an OV-17 column (II, 180°C) gave the following neutral compounds: 1,1-diphenylethane (0.032 mmol, 0.7 mole %, 2.1 min.), 1,2,3-triphenylpropane (0.007 mmol, 0.2 mole %, 14.9 min.), 2,2,3-triphenylpropane (0.003 mmol, 0.1 mole %, 15.9 min.), unknown* (0.004 mmol, 0.1 mole %, 16.9 min.), unknown* (0.008 mmol, 0.2 mole %, 24.1 min.), unknown** (0.052 mmol, 2.2 mole %, 51.7 min.). After distillation of the solvent through a twelve inch vigreux column, the weight of the crude acids was 1.1280 g and the weight of the neutral products was 0.5456 g.

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*The gc response factor for these compounds was assumed to be the same as triphenylpropane.

**This compound may be a tetraphenylbutane and thus has half the gc response factor of 1,1-diphenylethane.

CHAPTER V

DISCUSSION

Reaction of Cesium Alloys with Benzene and Alkylbenzenes

The results of the reaction of cesium alloys with benzene, toluene, m-xylene, p-xylene, and t-butylbenzene are tabulated in Table 3. In these reactions benzene, toluene, and m-xylene (and not p-xylene or t-butylbenzene) react with excess Cs-K-Na alloy at -45°C in THF (see Scheme 9) to form immediately a black precipitate (I) and then a yellow precipitate (II) which upon protonation gives a high yield of the dimer (III).

It has been found that in the reaction of cesium alloys with benzene that lowering the reaction temperature below the freezing point of Cs-K alloy reduces the product yield since the reactivity of the alloy is dependent upon rapid diffusion of cesium to the liquid alloy's surface. For example, in experiment III-127, the reaction of benzene with excess Cs-K alloy (fp = -37°C) in THF at -70°C for three hours and then at -25°C for three and a half hours gave after protonation cyclohexene (8.6 mole %), 1,4-dihydrobenzene (10.7 mole %), 1,1',4,4'-tetrahydrobiphenyl (3.5 mole %), and benzene (70.6 mole %). The yield of dimeric products is also diminished when the bulk of the reaction mixture including the excess cesium alloy is rapidly siphoned into ice water. For example, in experiment III-5, the reaction of benzene with excess Cs-K alloy in THF at -20°C for 4.3 hours gave after protonation

Table 3. Extent of Dimerization of Cesium Benzenide and Cesium Alkylbenzenides

Reaction Conditions	Yield Dimer (mole %)	Radical Anion Yield[a]
Benzene (III-15) Cs-K; -37° to -16°C; 5 hr.	32.4%	77.3%
Benzene (III-145) Cs-K; -18°C; 2 hr.	58.4%	91.9%
Benzene (III-153) Cs-K-Na; -45°C; 3 hr.	75.7%	93.5%
Benzene (3-162) Cs-sand; -75° to +5°C; 6 hr.	42.7%[c]	79.1[b,c]
Toluene (II-85) Cs-sand; -75° to -16°C; 3.5 hr.	10.2%[c]	21.3%[c]
Toluene (IV-51) Cs-K-Na; -45°C; 3 hr.	58.1%	89.1%
Toluene (IV-69) Cs-K-Na; -50°C; 4.5 hr.	47.2%	90.6%
p-xylene (IV-121) Cs-K-Na; -45° to +20°C; 22 hr.	0.1%[e]	0.5%
m-xylene (IV-123) Cs-K-Na; -48°C; 3.5 hr.	38.1%	83.3%
m-xylene (IV-131) Cs-K-Na; -48°C; 3 hr.	54.8%	81.6%
t-butylbenzene IV-79 Cs-K-Na; -40° to +67°C; 46 hr.[d]	0.7%[e]	26.8%

[a]The radical anion yields are based on the total observed reduction and dimerization products after hydrolysis.

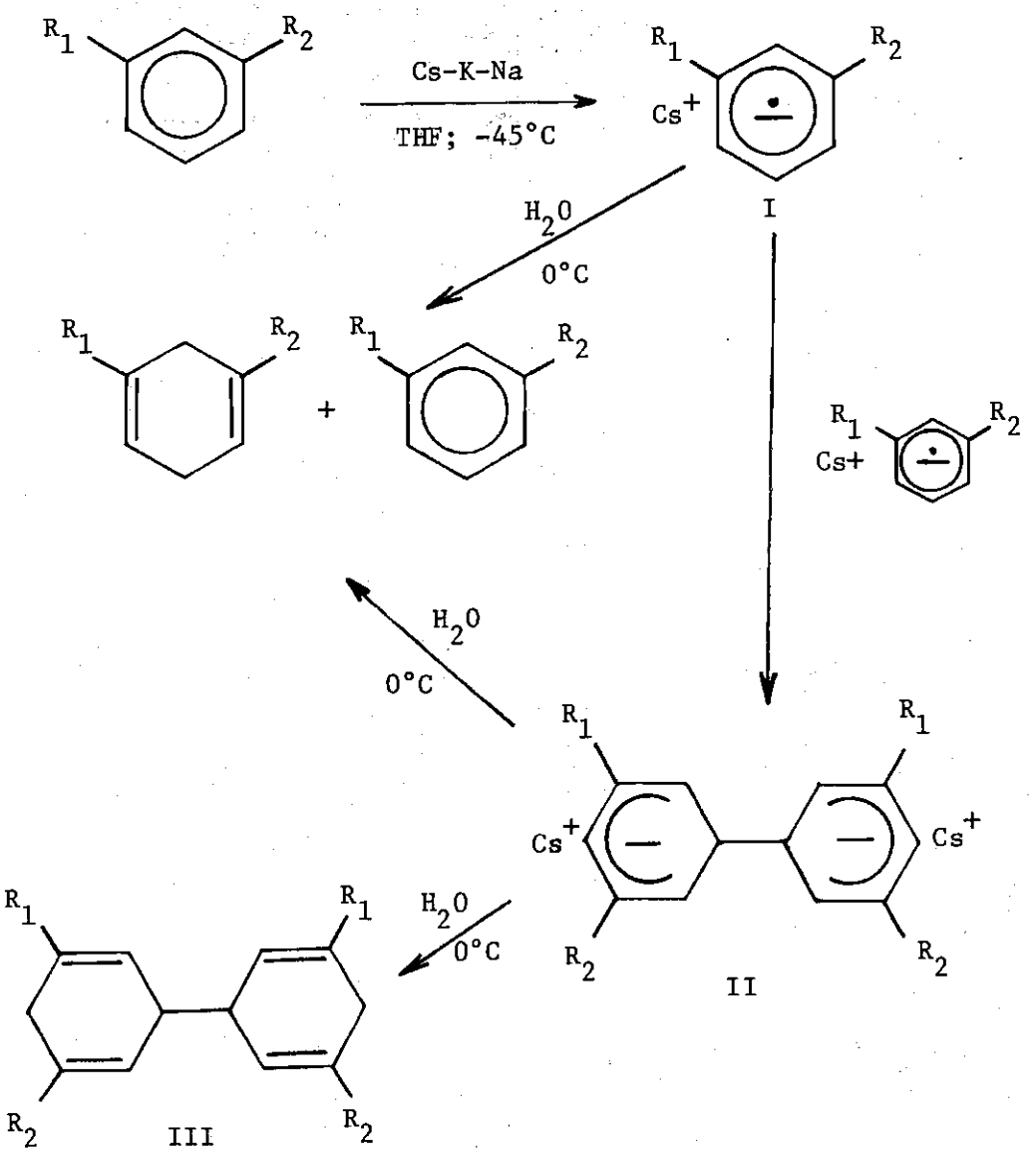
[b]This was Longfield's best yield of the benzene dimer. Reference 4, p. 70.

[c]These yields are based on cesium metal as the limiting reagent.

[d]The t-butylbenzene reacted after seven hours at 27°C; the reactive intermediate was rapidly protonated by the THF after raising the temperature to 67°C.

[e]The identity of the dimeric products, in view of the low yields, was based solely on gc retention times.

Scheme 9



benzene: $R_1 = R_2 = H$; III = 75.7%

toluene: $R_1 = CH_3$, $R_2 = H$; III = 56.3%

m-Xylene: $R_1 = R_2 = CH_3$, III = 54.8%

cyclohexene (52.2 mole %), 1,4-dihydrobenzene (7.3 mole %), 1,1'4,4'-tetrahydrobiphenyl (6.6 mole %) and benzene (32.5 mole %). Assuming that one alkali metal atom is required for each added proton in the products the extent of reduction is 230% as compared to 100% if only the organometallic had been protonated. In reaction III-145, which avoids the previous problems, benzene was reacted with excess Cs-K alloy in THF at -18°C for four hours. The alloy was allowed to settle to the bottom of the reaction flask. Then the reaction mixture was carefully jetted into ice water through a stainless steel canula. By slowly lowering the canula to the bottom of the reaction flask siphoning of the Cs-K alloy into the ice water was avoided. The composition of the protonation products was cyclohexene (2.6 mole %), 1,4-dihydrobenzene (11.6 mole %), 1,1',4,4'-tetrahydrobiphenyl (58.4 mole %), and benzene (19.2 mole %). In this reaction the starting alloy composition was found to be 74.6 atom % Cs and 25.4 atom % K. The final alloy composition was 54.5 atom % Cs and 45.5 atom % K. The calculated alloy composition based on the extent of reduction and dimerization of the organic products was 53.7 atom % Cs and 46.3 atom % K. Thus cesium metal is selectively extracted from the alloy by benzene. Thus the ratio of reacted cesium to benzene is 0.92:1.00 based on the organic products and 0.90:1.00 based on the alloy analysis.

In a more effective procedure (reaction III-153), benzene was reacted with excess Cs-K-Na alloy at -45°C in THF for three hours and the reaction mixture was carefully jetted into ice water. The composition of the protonation products was 1,4-dihydrobenzene (8.9 mole %),

1,1',4,4'-tetrahydrobiphenyl (75.7 mole %), and benzene (14.6 mole %). The composition of the alloy before and after reaction indicates that cesium is selectively extracted from the Cs-K-Na alloy by benzene (see Table 4). Thus the ratio of reacted cesium to benzene is 0.94:1.00 based on the organic products and 0.87:1.00 based on the alloy analysis. This data indicates that the reaction proceeds toward the theoretical ratio of one cesium atom reacting with each benzene ring and that only a small amount of additional reduction occurs during protonation.

Under identical conditions to those which gave the highest yield of the benzene dimer, toluene reacts with Cs-K-Na alloy to form the corresponding radical anion which dimerizes to the dianion which gives after protonation a 45.4 mole % (in reaction IV-69) to a 56.3 mole % yield (in reaction IV-51) of 3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl (see Table 5). Dehydrogenation of this dimer with excess DDQ gave 3,3-'dimethylbiphenyl (99.1%), 2,3'-dimethylbiphenyl (0.7%) and 2,2'-dimethylbiphenyl (0.2%). Thus the dimerization of cesium toluenide favors coupling of the radical anion at the position meta to the methyl group by 99.5%. The esr spectrum of the toluene radical anion can be interpreted in terms of the HOMO structure IV,[66] dimerization of the radical anion would be expected to take place at the positions of highest electron spin density, hence at the ortho or meta positions. However, dimerization takes place preferentially at the meta position since

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[66]L. Salem, "The Molecular Orbital Theory of Conjugated Systems." W. A. Benjamin Inc., New York, 1966, p. 257.

Table 4. Analysis of the Cesium Alloys for the Reacting Alkali Metal in the Reactions of Benzene and Toluene

Reaction	Composition of the Alloy in Atom %		
	Initial	Final	Calculated
Benzene (II-122)	78.6% Cs	58.5% Cs	66.7% Cs[1]
	21.4% K	41.5% K	33.3% K
Benzene (III-145)	74.6% Cs	54.5% Cs	53.7% Cs[1]
	25.4% K	45.5% K	46.3% K
Benzene (III-45)	47.6% Cs	38.9% Cs	35.5% Cs[2]
	40.3% K	49.9% K	49.6% K
	12.1% Na	11.2% Na	14.9% Na
Benzene (III-153)	42.1% Cs	33.9% Cs	33.3% Cs[1]
	48.9% K	55.7% K	56.4% K
	9.0% Na	10.4% Na	10.3% Na
Toluene (IV-69)	48.3% Cs	37.8% Cs	39.3% Cs[1]
	44.5% K	53.2% K	52.3% K
	7.2% Na	9.0% Na	8.4% Na

[1]The calculated alloy composition is based on the extent of reduction of the organic products assuming only cesium metal reacts.

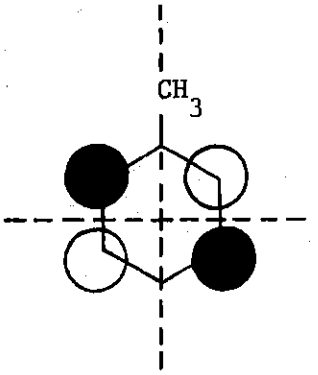
[2]This calculated alloy composition was based on a postulated reaction of one cesium atom per benzene ring.

Table 5. Analysis of the Products of the Reaction of Toluene with Cs-K-Na Alloy or Cesium Sand

Products	Reaction Yields (mole %)		
	Reaction IV-51 Cs-K-Na -45°C; 3.0 hr.	Reaction IV-69 Cs-K-Na -45°C; 4.5 hr.	Reaction II-85 Cesium sand -75° to -16°C; 3.5 hr.
2,5-dihydrotoluene	15.6%	21.6%	11.1%[a]
toluene	23.2%	31.2%	excess
3,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl	56.3%	45.4%[b]	10.2%[a]
3,3'-dimethyl-1,1',2,4'-tetrahydrobiphenyl and/or 3,3'-dimethyl-1,1',4,6'-tetrahydrobiphenyl	1.7%	1.8%	---

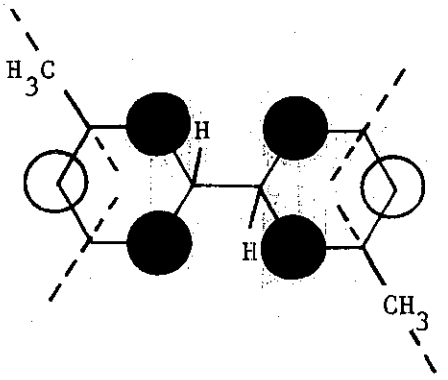
[a]These yields are based on Cs as the limiting reagent.

[b]This yield includes a 0.16 mole % yield of 2,3'-dimethyl-1,1',4,4'-tetrahydrobiphenyl and a 0.005 mole % yield of 2,2'-dimethyl-1,1',4,4'-tetrahydrobiphenyl.



IV

this process leads to the most stable anion V when the methyl group is at a nodal position in the HOMO (and hence destabilize the anion as little as possible). The spectroscopic evidence which proves that



V

the aromatized toluene dimer, IV-69-DDQ, is 3,3'-dimethylbiphenyl is summarized in Tables 6 and 7 and Figures 8 and 9. In reaction IV-69, analysis of the Cs-K-Na alloy before and after reaction shows that toluene like benzene selectively extracts cesium metal from the liquid alloy to form cesium toluenide (see Table 3). Thus the ratio of reacted cesium to toluene is 0.91:1.00 based on the organic products and

Table 6. Comparison of the UV Spectra (95% EtOH) of Aromatized Toluene Dimer (IV-69-DDQ) and Aromatized m-Xylene Dimer (IV-131-DDQ) with Isomeric Dimethylbiphenyls (DMB)

	Compound	λ(Å)	ε
1)	IV-69-DDQ		
	(3,3'-dimethylbiphenyl)	2500	15,856
2)	3,3'-dimethylbiphenyl	2500	17,492
3)	2,3'-dimethylbiphenyl	2375	11,210
4)	2,2'-dimethylbiphenyl	2280 (shoulder)	30,433
5)	4,4'-dimethylbiphenyl	2550	22,158
6)	IV-131-DDQ		
	(3,3',5,5'-tetramethylbiphenyl)	2550	15,670

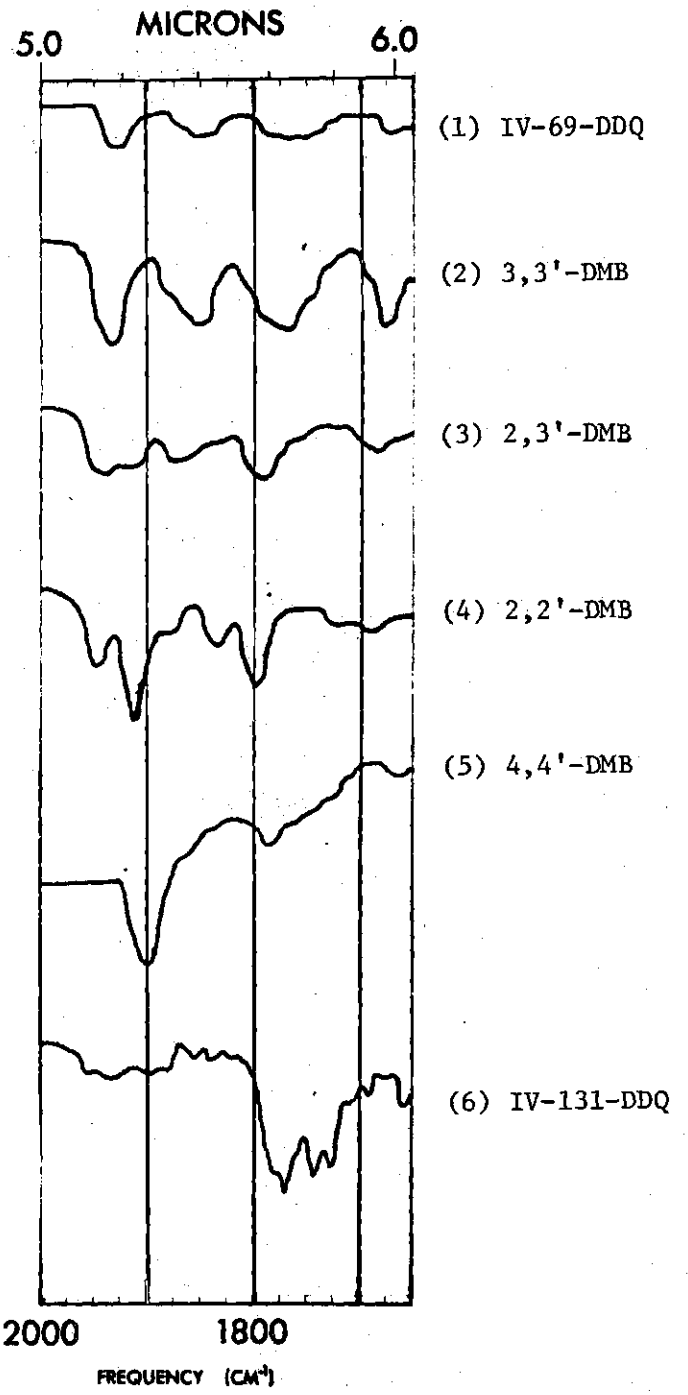


Figure 8. IR Spectra (Neat) of the 5.0 to 6.0 Micron Region for the Compounds Listed in Table 6.

Table 7. Comparison of the ^{1}H NMR (CCl_4) of the Aromatized Toluene Dimer (IV-69-DDQ) and the Aromatized m-Xylene Dimer (IV-131-DDQ) with Isomeric Dimethylbiphenyls

1) IV-69-DDQ (3,3'-dimethylbiphenyl):

δ 2.35 (6.0 H, s, methyl) and 7.18 (7.9 H, m, aromatic).

2) 3,3'-dimethylbiphenyl (3,3'-DMB):

δ 2.35 (6.0 H, s, methyl) and 7.18 (7.8 H, m, aromatic).

3) 2,3'-dimethylbiphenyl (2,3'-DMB):

δ 2.20 (3.0 H, s, o-methyl), 2.33 (3.0 H, s, m-methyl) and 7.1 (7.9 H, m, aromatic).

4) 2,2'-dimethylbiphenyl (2,2'-DMB):

δ 2.00 (6.0 H, s, methyl) and 7.08 (8.0 H, m, aromatic).

5) 4,4'-dimethylbiphenyl (4,4'-DMB):

δ 2.32 (6.0 H, s, methyl) and 7.23 (8.1 H, q, aromatic).

6) IV-131-DDQ (3,3',5,5'-tetramethylbiphenyl):

δ 2.3 (12.0 H, s, methyl), 6.8 (2.0 H, s, p, aromatic), and 7.07 (4.0 H, s, o-aromatic).

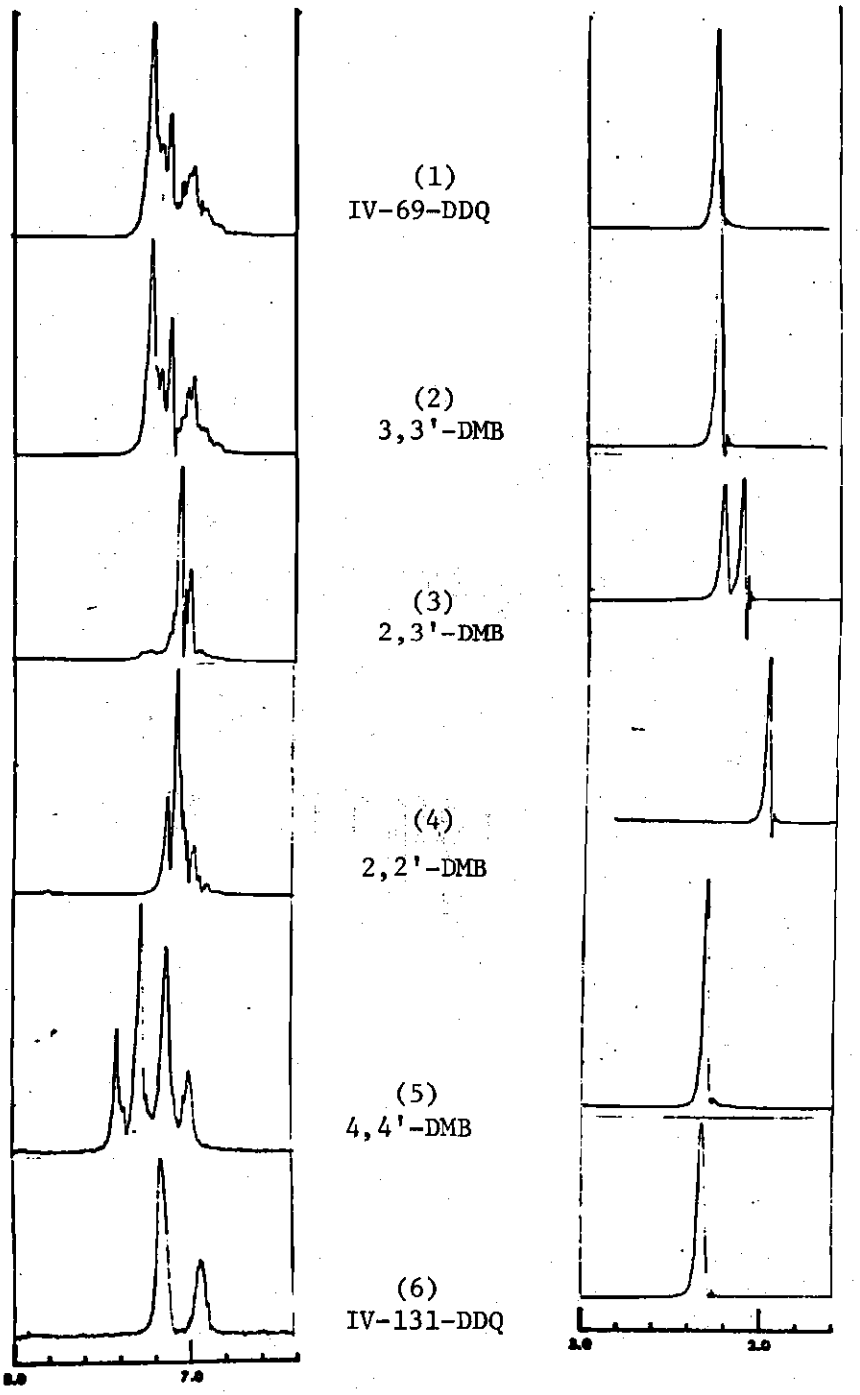
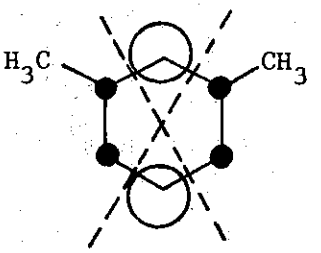


Figure 9. ^{1}H NMR (CCl_4) Spectra of the Compounds Listed in Table 7.

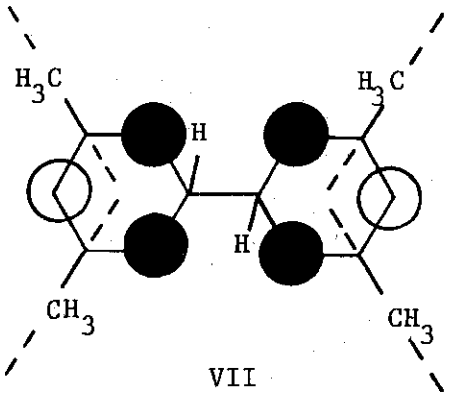
1.00:1.00 based on the alloy analysis.

Like benzene and toluene, m-xylene reacts with excess Cs-K-Na alloy in THF at -48°C to give the m-xylene radical anion which largely dimerizes. Thus after protonation there is a 54.8 mole % yield of 3,3',5,5'-tetramethyl-1,1',4,4'-tetrahydrobiphenyl (see Table 8). Thus the dimerization of cesium m-xylenide favors coupling at the position meta to both methyl groups. This can be understood since dimerization of the m-xylene radical anion (i.e., HOMO structure VI) would be



VI

expected to take place at the positions of highest electron spin density. Dimerization takes place at the position meta to both methyl groups since this process leads to the most stable anion VII when the methyl groups are at the nodal positions in the HOMO (and hence destabilize the anion as little as possible).

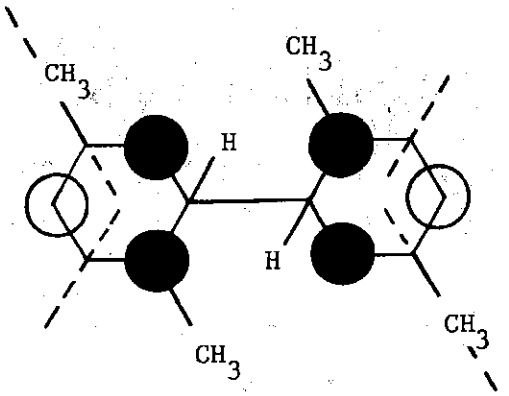


VII

Table 8. Analysis of the Products of the Reaction of m-xylene with Cs-K-Na Alloy

Product	Reaction Yields (mole %)	
	IV-123	IV-131
2,5-dihydro-m-xylene	22.6%	13.4%
m-xylene	39.3%	27.7%
3,3',5,5'-tetramethyl-1,1',4,4'-tetrahydrobiphenyl	38.1%	54.8%

Unlike m-xylene, p-xylene does not react with excess Cs-K-Na alloy at -45°C in THF. This may be due to the fact that the HOMO of anion VIII formed by the dimerization of the p-xylene radical anion is destabilized by having two methyl groups on carbons bearing excess negative change.



VIII

Unlike toluene, t-butylbenzene does not react with excess Cs-K-Na alloy in THF at -45°C. This is not surprising since t-butylbenzene is 25 times less stable as a radical anion than toluene.[29] However since it is known that cesium forms contact ion pairs in THF with anions[67] and that the potassium cation in the radical anion of [2.2]paracyclophane is centered above the aromatic ring,[68] the bulky t-butyl group in t-butylbenzene must interfere with the approach of the cesium atom to the cloud of the benzene ring. In Figure 10, two models are proposed to

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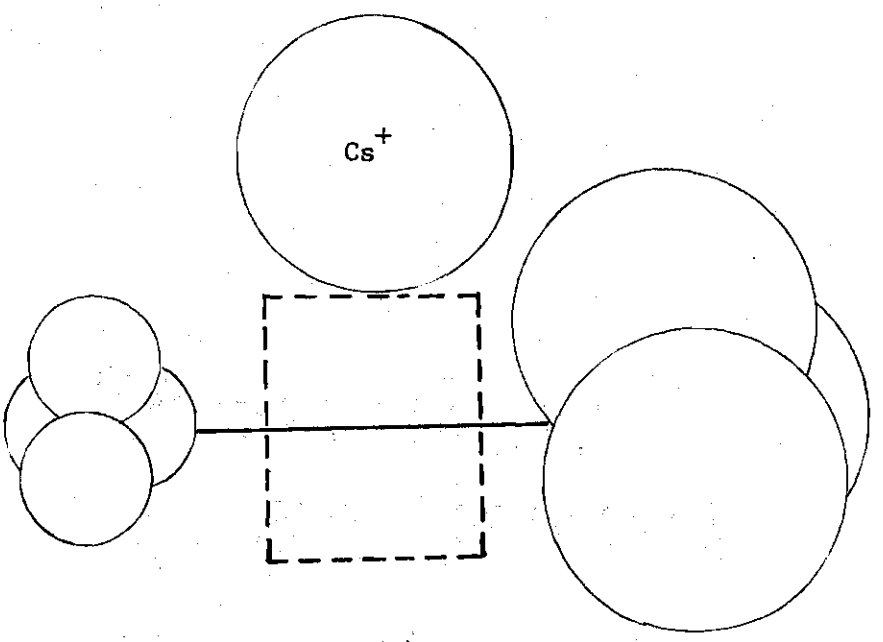
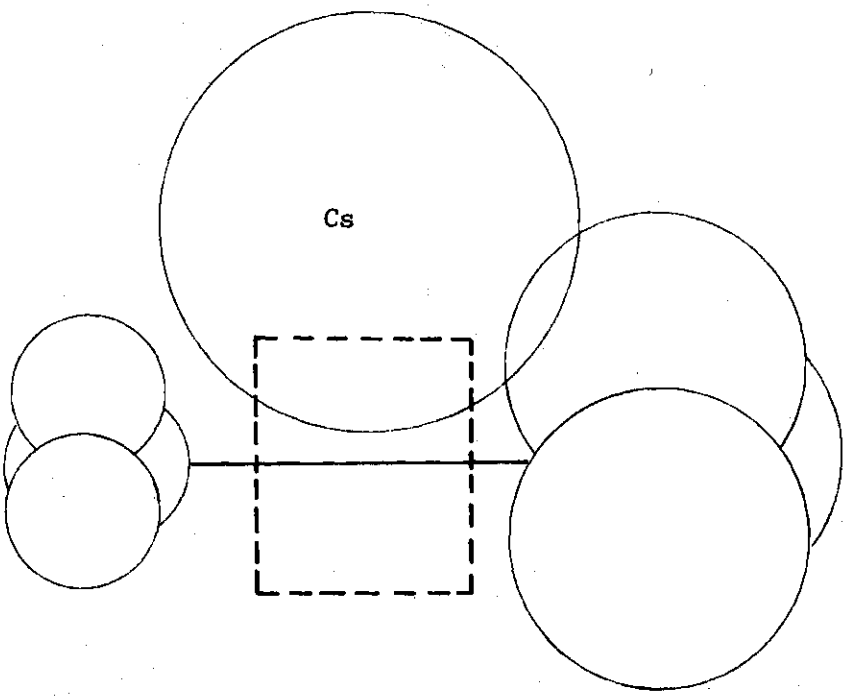
[67] T. E. Hogen-Esch and J. Smid, J. Amer. Chem. Soc., 88, 307 (1966).

[68] F. Gerson, W. B. Martin, Jr., and C. Wydler, Helv. Chim. Acta., 59, 1365 (1976).



(1)



(2)

Figure 10. Bonding Model for the Interaction of Cesium with a Methyl Group (left) and a t-Butyl Group (right on a Benzene Ring.

show the interaction of cesium with a methyl group (left) and a t-butyl-group (right) on a benzene ring. In model 1, a cesium cation (radius 1.69 Å) is bonded to an aryl radical anion at the half thickness (1.70 Å) of a benzene ring.[69] In this model there is little interference of the cesium cation with the bulky t-butyl group. However in model 2, the cesium atom (radius 2.67 Å) is shown penetrating the benzene ring in a manner analogous to that of the chromium atom in chromacene. Thus the distance between the surface of the metal and the plane of the benzene ring is 0.34 Å as in chromocene.[70] In model 2, there is considerable interaction between the cesium atom and the bulky t-butyl group which could interfere or prevent the formation of the radical anion. The truth likely lies between these two extreme models since it has been shown by Szwarc and coworkers[71] that the radius of a cesium cation in THF at -45°C is 2.45 Å. In similar work, Hogen-Esch and Smid[72] have shown that the center to center distance in fluorenylcesium is 3.76 Å. At -45°C the distance from the surface of the cesium cation to the plane of the benzene ring could be 1.31 Å based on the previous work. However even at this distance, the cesium cation of radius 2.45 Å would slightly overlap the bulky t-butyl group. Yet as the temperature is raised from -45°C to 25°C the effective radius of cesium in THF decreases from 2.45 Å

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[69] L. Pauling, "Nature of the Chemical Bond." Cornell Univ. Press, Ithaca, N.Y., 1960, p. 260.

[70] G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds." Volume 2, Methuen & Co. LTD, London, 1968, p. 171.

[71] C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, J. Amer. Chem. Soc., 87, 5548 (1965).

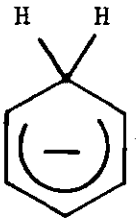
[72] T. E. Hogen-Esch and J. Smid, J. Amer. Chem. Soc., 88, 318 (1966).

to 2.25 Å. This would eliminate the interaction of the cesium cation and the t-butyl group and may explain why t-butylbenzene does react at 27°C with Cs-K-Na alloy in THF to form a black precipitate which gives a 13.1 mole % yield of 2,5-dihydro-t-butylbenzene and 0.7 mole % yield of dimers after protonation.

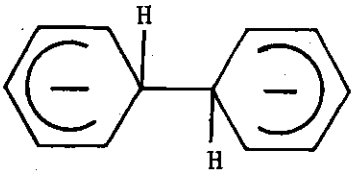
Reactions of Cesium Benzenide and Cesium m-Xylenide in the Presence of 18-Crown-6

In reaction II-53, the addition of one molar equivalent of 18-crown-6 to the black precipitate of cesium benzenide from the reaction of cesium sand with benzene in THF at -70° gives after warming to 5° with stirring for one hour a bright red precipitate in a deep red solution. Protonation of this solution with ice water gave an almost quantitative yield of cyclohexene and 1,4-dihydrobenzene and only a trace of 1,1',4,4'-tetrahydrobiphenyl. These results are very different from those of protonation of the expected (at -5°C) yellow dimerization product, which gives mainly 1,1',4,4'-tetrahydrobiphenyl. It is possible that the red color is due to protonation of cesium benzenide by the 18-crown-6 to give the red pentadienyl anion IX. According to mass spectral analysis, in reaction II-157, the 1,4-dihydrobenzene obtained from the quenching of the red anion into partially frozen deuterium oxide consisted of a 0.47:1.00 ratio of 1,4-cyclohexadiene-3d from anion IX to 1,4-cyclohexadiene-3d-6d from the radical anion.

In reaction IV-161, the reaction of benzene with Cs-K-Na alloy in THF at -43°C in the presence of two molar equivalents of 18-crown-6 gave upon carbonation after five hours and dehydrogenation by DDQ 16.8 mole %



IX



X

yield of product (benzoic acid) which largely is derived from the cyclohexadienyl anion IX, 3.6 mole % of products (phthalic and terephthalic acids) which are derived from the benzene radical anion, and 17.6 mole % of product (largely o,o'-,o,p'-, and p,p'-biphenyldicarboxylic acids) derived from the dimer X of the benzene radical anion. Thus the ratio of products derived from the pentadienyl anion, radical anion, and dimer are in the ratio of 0.96:0.21:1.00. In the absence of the 18-crown-6 the ratio of these products would be 0.09:1.00:0.68,[73] hence considerable amount of the radical anion had to be protonated by the 18-crown-6 to account for the large amount of benzoic acid derived in this reaction.

The reaction of m-xylene with Cs-K-Na alloy in THF at -40°C in the presence of one molar equivalent of 18-crown-6 gave on protonation after some three hours only monomeric hydrocarbons. For reaction IV-147, which was quenched with deuterium oxide, 63.6 mole % of 2,5-dihydro-m-xylene and 33.4 mole % m-xylene was obtained. According to ^{1}H and ^{13}C NMR analysis, the 2,5-dihydro-m-xylene was monodeuterated and consisted of a 1.00:3.74 ratio of XI to XII. In reaction IV-157 with two molar equivalents of 18-crown-6 per mole of m-xylene, the acidic

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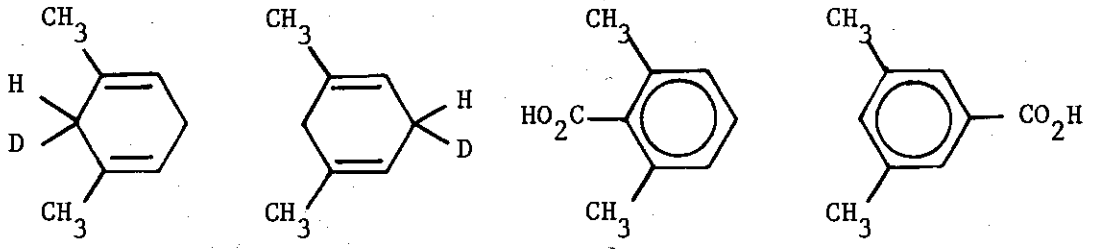
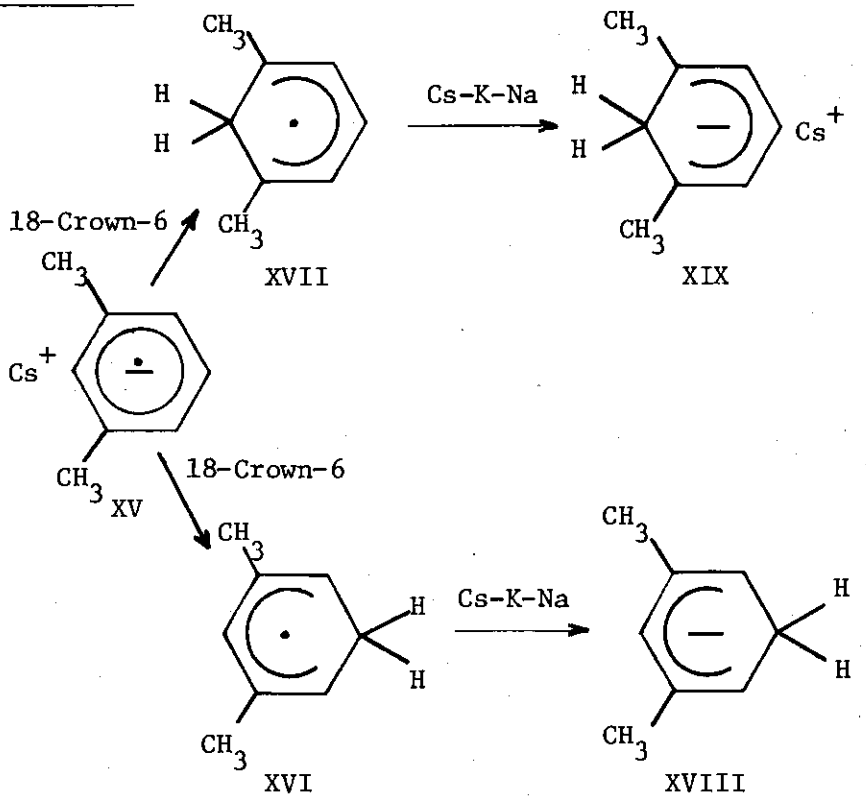
[73]Reference 4, p. 80.

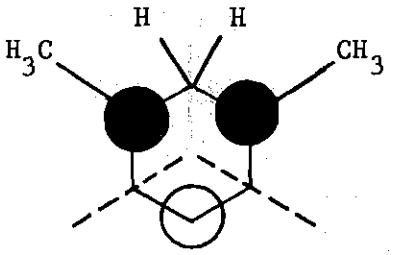


product from carbonation and dehydrogenation consisted of about a 1.00:3.86 ratio of XIII to XIV. This data is in good agreement with the conclusion that 18-crown-6 protonates the radical anion XV to give about a 1.0:3.8 ratio of radicals XVI and XVII which are reduced to the corresponding ratio of the anions XVIII and XIX. Protonation like

Scheme 10



dimerization of the radical anion would be expected to take place at the positions of highest electron spin density in HOMO structure VI, hence at positions ortho or meta to both methyl groups. While dimerization takes place preferentially at the meta position since this process leads to the most stable anion VII, protonation occurs preferentially at the position ortho to both methyl groups since this process leads to the most stable radical XVII where the methyl groups are all at centers of high spin density in HOMO XX (and hence stabilize the radical as much as possible). The higher regiospecificity in dimerization than in



XX

protonation is due to the larger effect of methyl groups in destabilizing anions than in stabilizing radicals in solution. Thus while somewhat less than half of the benzene radical anion was protonated by 18-crown-6, the m-xylene radical anion was completely protonated. These comparative results may be understood on the basis that methyl groups destabilize radical anions and increase their rate of protonation by 18-crown-6.

Reaction of Biphenyl with Cs-K Alloy

As shown in scheme 5, cesium metal reacts with biphenyl in THF at

35°C to give the biphenyl dianion.[24] Since the products obtained by the hydrolysis of this reaction are the same as those obtained from the reaction of biphenyl with Na-K alloy in DME[74] or the reaction of biphenyl with lithium metal in liquid ammonia,[75] analysis of Cs-K alloy for the alkali metal which reacts with biphenyl should establish whether or not cesium has a superior reducing power in THF over the other alkali metals in a system which any of the alkali metals can reduce.

The reaction of biphenyl with excess Cs-K alloy in THF at 25°C gives after careful hydrolysis the products shown in Scheme 5 and Table 9. The alloy analysis data in Table 10 indicates that cesium metal was extracted preferentially from the alloy. However this data indicates that not enough cesium was extracted to account for the reduction of the products. In reaction III-101, the ratio of reacted metal to biphenyl is 1.94:1.00 based on the organic products and 1.63:1.00 based on the alloy analysis assuming only fractionation of cesium metal. On the same basis in reaction III-115, the ratios are 1.89:1.00 and 1.42:1.00 respectively. Since both ratios should approach a 2.0:1.0 theoretical ratio of reacted metal to biphenyl, it is possible that some potassium does react. In reaction III-101, if both potassium and cesium were extracted from the initial alloy to give a final alloy of 53.2 atom % Cs and 46.8 atom % K and a ratio of reacted metal to biphenyl equal to that obtained from the organic products (i.e., 1.94:1.00) then the ratio of reacted cesium to potassium would be 12.53:1.00. Using the same

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[74] S. A. DeLicastro and M. A. Ruveda, J. Organometal. Chem., 39, 225 (1972).

[75] A. J. Birch and G. Nadamuni, J. Chem. Soc., Perkin Trans., 1, 545 (1974).

Table 9. Analysis of the Products of the Reaction of Biphenyl with Cs-K Alloy

Product	Reaction Yields (mole %)		
	III-101	III-115	IV-19*
Cyclohexene	1.4%	---	---
Benzene	3.3%	1.4%	---
Phenylcyclohexane	0.4%	0.7%	---
3-phenylcyclohexene	8.2%	6.8%	5.4%
1,4-dihydrobiphenyl	52.8%	54.5%	35.8%
1-phenylcyclohexene	4.5%	3.0%	3.3%
3,4-dihydrobiphenyl	6.7%	7.9%	3.1%
Biphenyl	22.6%	16.4%	15.0%

*The flask rinse contained 29.0 mole % of biphenyl reduction products and 2.7 mole % of cyclohexene and benzene.

Table 10. Analysis of the Cesium Alloys for the Reacting Alkali Metal in the Reactions of Biphenyl, 2,2-Diphenylpropane, and 1,1,1-Triphenylethane

Reaction	Composition of the Alloy in Atom %		
	Initial	Final	Calculated
Biphenyl (III-101)	63.7% Cs	53.2% Cs	51.4% Cs[1]
	36.3% K	46.8% K	48.6% K
Biphenyl (III-115)	59.6% Cs	53.7% Cs	52.3% Cs[1]
	40.4% K	46.3% K	47.7% K
2,2-diphenylpropane (II-91)	53.6% Cs	41.1% Cs	39.5% Cs[2]
	46.4% K	58.9% K	60.5% K
1,1,1-triphenylethane (IV-41)	47.4% Cs	43.0% Cs	43.9% Cs[1]
	47.5% K	49.7% K	50.7% K
	5.1% Na	7.3% Na	5.4% Na
1,1,1-triphenylethane (IV-55)	46.6% Cs	40.1% Cs	41.9% Cs[2]
	50.2% K	56.5% K	54.7% K
	3.2% Na	3.4% Na	3.4% Na

[1]The calculated alloy composition is based on the extent of reduction or intramolecular cyclization of the organic products and assumes that only cesium metal reacts.

[2]This calculated alloy composition was based on a postulated reaction of one cesium atom per benzene ring.

assumptions, the ratio would be 7.76:1.00 in reaction III-115. Thus the ratio of cesium to potassium extracted from Cs-K alloy by biphenyl is on the average 10:1 in THF at room temperature and is proof of the superior reducing ability of cesium metal.

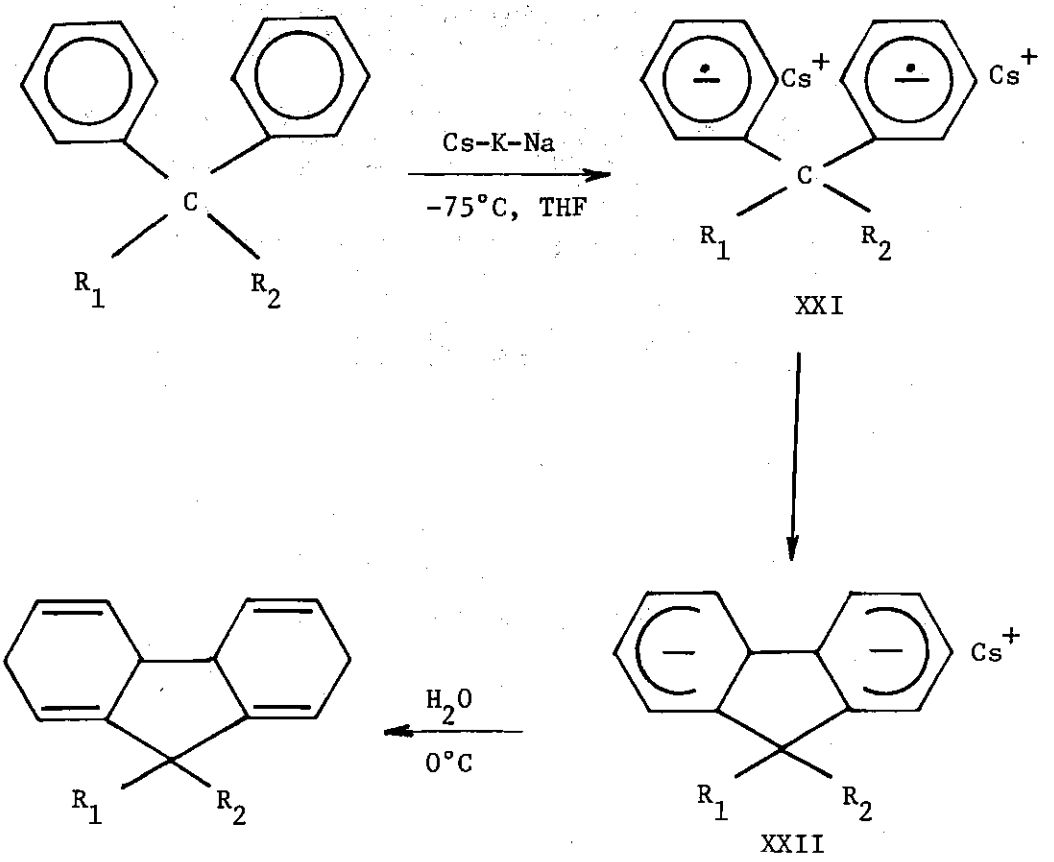
Reaction of Diphenylmethane, 2,2-Diphenylpropane, 1,1,1-Triphenylethane and 1,3-Diphenylpropane with Cesium Alloys

In reaction IV-135, the products from the reaction of diphenylmethane with Cs-K-Na alloy in THF at -75°C were quenched in ice water and dehydrogenated with excess DDQ. Analysis by gc and ^{1}H NMR indicated that only diphenylmethane and no flourene was present in the dehydrogenated material. This experiment confirms the result reported by Longfield[9] that dehydrogenation of the products, from the reaction of Cs-K-Na alloy with diphenylmethane, with Pd/C gives no fluorene (see Scheme 2).* Thus diphenylmethane unlike 2,2-diphenylpropane and 1,1,1-triphenylethane does not react with Cs-K-Na alloy at -75°C to undergo intramolecular cyclization to give a near quantitative yield of a tetrahydrofluorene derivative as shown in Scheme 11.

The diradical anion XXI and the dianion XXII are depicted as cesium compounds since alloy analysis of the reaction of both 2,2-diphenylpropane with Cs-K alloy and 1,1,1-triphenylethane with Cs-K-Na alloy shows that cesium metal was preferentially extracted from the respective alloy

*However the low yield (24.9%) of 2,5-dihydrodiphenylmethane, which corresponds to the major product being likely a monoradical anion, suggests that the yield of diradical (XXI) may have been too low to give detectable fluorene derivative.

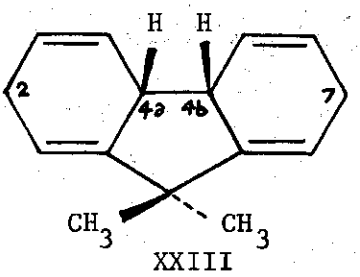
Scheme 11



where: $R_1 = R_2 = CH_3$ for 2,2-diphenylpropane

$R_1 = CH_3$ and R_2 = Ph for 1,1,1-triphenylethane

(see Table 10). The yield of XXIII from the reaction of 2,2-diphenylpropane with Cs-K-Na in THF at -75°C for three hours was found to be 89.9 mole % (reaction IV-143). This result therefore establishes that a near quantitative yield of cis-9,9-dimethyl-2,4a,4b,7-tetrahydrofluorene, XXIII, is derived from this reaction and confirms Longfield's qualitative assertion[7] that XXIII was obtained in high yield. The ^1H NMR spectrum of XXIII shows that the methyl groups at C-9 are non-equivalent



XXIII

and thus establishes the cis-fused nature of XXIII, since the trans-fused compound would have equivalent methyl groups due to a two fold axis of symmetry thru C-9.[76] This ^{1}H NMR analysis has now been confirmed by ^{13}C NMR which shows two non-equivalent methyl groups (see Figure 7). Models suggest that the methyl which is down has an environment very similar to that of the allyl bridgehead carbons 4a and 4b and thus should be considerably deshielded. In fact ^{13}C NMR analysis indicates that the carbon of this methyl has absorbance at 26.0 δ which is very close to that of 26.9 δ for the allyl carbons at positions 2 and 7; the carbon of this methyl is deshielded relative to the carbon at 22.4 δ for the methyl which is up.

The yields of fluorene derivatives from the previously cited reactions are summarized in Table 11. It is to be noted that the mild temperatures necessary for effective sampling and analysis of cesium alloys and dimerization of benzene results in reduced yields of the fluorene derivatives relative to the values which have previously been reported.[6,7]

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[76]Reference 4, p. 195.

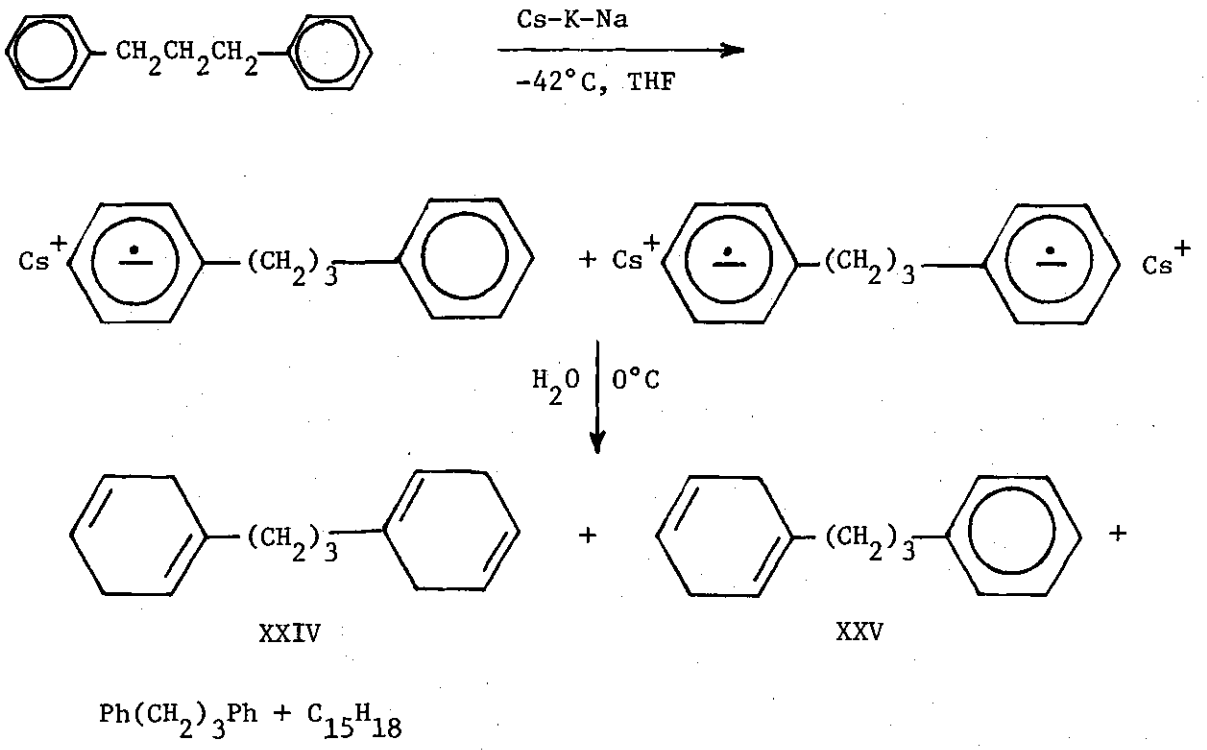
Table 11. Yield of Fluorene Derivatives from the Reaction of Polyphenylmethanes with Cesium Alloys

Reaction Conditions	Fluorene derivative, mole % yield	
diphenylmethane (IV-135) Cs-K-Na; -75°C; 2 hr.	---[a]	---[a]
2,2-diphenylpropane (II-91) Cs-K; -34°C to -20°C; 3 hr.	cis-9,9-dimethyl-2,4a,4b,7-tetrahydrofluorene	25.1%
2,2-diphenylpropane (IV-143) Cs-K-Na; -75°C; 3 hr.	cis-9,9-dimethyl-2,4a,4b,7-tetrahydrofluorene	89.9%
1,1,1-triphenylethane (IV-41) Cs-K-Na; -50°C; 1.5 hr.	9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene	66.9%
1,1,1-triphenylethane (IV-55) Cs-K-Na; -50°C; 3.5 hr.	9-methyl-9-phenyl-2,4a,4b,7-tetrahydrofluorene	71.7%

[a]The major products of this reaction were diphenylmethane (67.7%) and 2,5-dihydrodiphenylmethane (24.9%). No fluorene derivative was formed in this reaction.

The reaction of 1,3-diphenylpropane with cesium alloys is similar to that of diphenylmethane in that only ring reduction products are observed. For example in reaction IV-5, which is shown in Scheme 12, hydrolysis of the products from the reaction of 1,3-diphenylpropane with Cs-K-Na alloy at -42°C for 21 hours gave mainly 1,3-bis(2',5'-dihydrophenyl)propane (XXIV) (31.8 mole %) and 1-(2',5'-dihydrophenyl)-3-phenylpropane (XXV) (33.5 mole %). Since the radical anion yield as measured by ESR spectroscopy was 31.5% (based on the available number of aromatic rings) and quenching with iodine resulted in a quantitative recovery of 1,3-diphenylpropane, the reaction must proceed through a radical anion as shown in Scheme 12 (see reaction I-112). The data in Table 12 proves

Scheme 12



XXIV XXV

$Ph(CH_2)_3Ph + C_{15}H_{18}$

Table 12. Analysis of the Cesium Alloys for the Reacting Alkali Metal in the Reaction of 1,3-Diphenylpropane

Reaction	Composition of the alloy in atom %		
	Initial	Final	Calculated
1,3-diphenylpropane (I-112)	43.6% Cs[3]	33.9% Cs[3]	33.4% Cs[1]
	42.6% K	49.8% K	50.4% K
	13.8% Na	16.3% Na	16.2% Na
1,3-diphenylpropane (II-15)	56.6% Cs[3]	42.9% Cs[3]	40.4% Cs
	39.8% K	48.0% K	54.7% K
	3.6% Na	9.1% Na	4.9% Na
1,3-diphenylpropane (II-115)	67.2% Cs	51.7% Cs	52.5% Cs[2]
	32.8% K	48.3% K	47.5% K
1,3-diphenylpropane (III-137)	76.8% Cs	54.2% Cs	52.4% Cs[1]
	23.2% K	45.8% K	47.6% K
1,3-diphenylpropane (IV-5)	41.8% Cs	35.2% Cs	33.6% Cs[1]
	48.2% K	53.3% K	55.0% K
	10.0% Na	11.5% Na	11.4% Na

[1]The calculated alloy composition is based on the extent of reduction of the organic products and the assumption that only cesium reacts.

[2]This calculated alloy composition was based on a postulated reaction of one cesium atom per benzene ring.

[3]These analyses were done with use of Flame Emission Spectroscopy.

that 1,3-diphenylpropane like the previously discussed hydrocarbons preferentially extracts cesium metal from both Cs-K and Cs-K-Na alloy. The first two alloy analyses in Table 11 were done with use of flame emission spectroscopy and show the same trend as the analyses by titrimetric and gravimetric techniques.

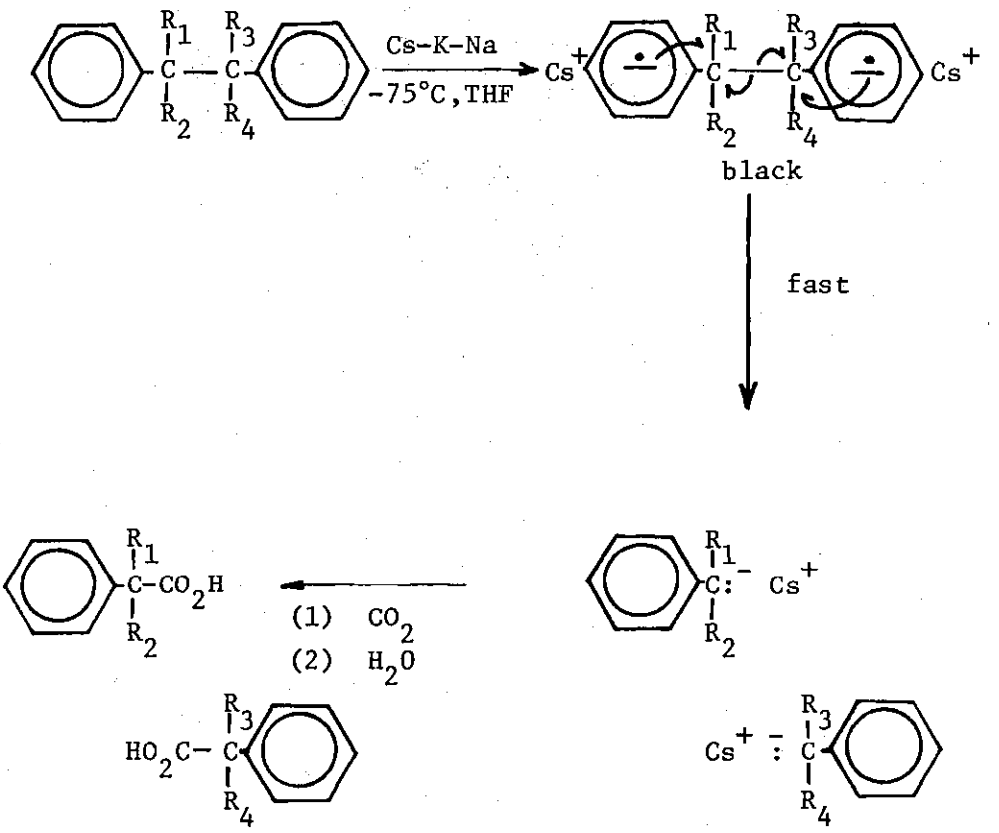
The Cleavage of Bibenzyl, 1,2-Di-p-tolyethane, 2,3-Dimethyl-2,3-diphenylbutane, and 1,2,2-Triphenylpropane with Cs-K-Na Alloy

In reaction IV-83, hydrolysis of the product from the reaction of bibenzyl with Cs-K-Na alloy in THF at -75°C for 1.5 hours gave a 95.1 mole % yield of toluene. Thus instead of undergoing intramolecular cyclization or side chain metallation, bibenzyl evidently forms a diradical anion which then cleaves to benzylcesium. This interpretation was confirmed in reaction IV-93 in which part of the orange-red benzyl cesium was carbonated to give phenylacetic acid (see Scheme 13).

In reaction IV-97, 2,3-dimethyl-2,3-diphenylbutane was reacted with Cs-K-Na alloy for 2.5 hours at -75°C. The red product was carbonated to give α,α-dimethylphenylacetic acid. This reaction visually appeared to proceed faster than the reaction of bibenzyl. Thus the addition of methyls to bibenzyl may sterically accelerate the cleavage reaction.

In reaction IV-115, 1,2,2-triphenylpropane was reacted with Cs-K-Na alloy for 1.25 hours at -75°C. The red products were carbonated to give a 1:1 mixture of phenylacetic acid and 2,2-diphenylpropionic acid.

Scheme 13



where (a) $R_1 = H = R_2 = R_3 = R_4$

(b) $R_1 = CH_3 = R_2 = R_3 = R_4$

(c) $R_1 = R_2 = H$; $R_3 = CH_3$; $R_4 = Ph$

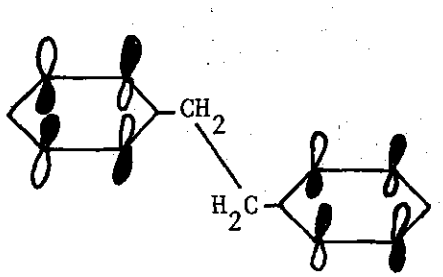
Thus as indicated in Table 13, the cleavage of bibenzyl and related compounds by Cs-K-Na alloy at -75°C in THF is a general reaction which results in a quantitative yield of benzylic anions. The cleavage of the bibenzyl diradical anion can be rationalized by the observation that the unpaired electrons in the diradical anion could be in HOMO XXVI or XXVII. In XXVII an electron rich p-orbital can overlap the sp^3 bonding

Table 13. The Products from Cleavage of Bibenzyl and Related Compounds by Cs-K-Na Alloy

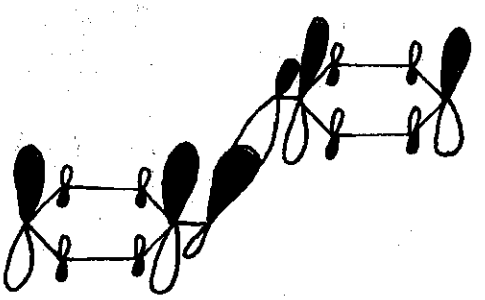
Reaction	Cleavage product[1] (mole %)	
Bibenzyl (IV-101)	phenylacetic acid	93.4%
-75°C; 1.5 hour	toluene	4.4%
1,2-di-p-tolylethane[2] (IV-125)	p-tolylacetic acid	6.2%
-75° to +12°C; 5 hours	p-xylene	0.1%
2,3-dimethyl-2,3-diphenylbutane (IV-97) -75°C; 2.5 hours	α,α-dimethylphenylacetic acid	99.0%
	cumene	0.7%
1,2,2-triphenylpropane (IV-115)	phenylacetic acid	84.8%
-75°; 1.25 hours	toluene	11.5%
	2,2-diphenylpropionic acid	87.3%
	1,1-diphenylethane	8.2%

[1]The products of these reactions were carbonated to derivatize the carbanions formed by the cleavage of the benzylic bond.

[2]The yield of acids in this reaction was 91 wt. %, the major products were diacids derived from benzyl and sidechain metallation of 1,2-di-p-tolylethane.

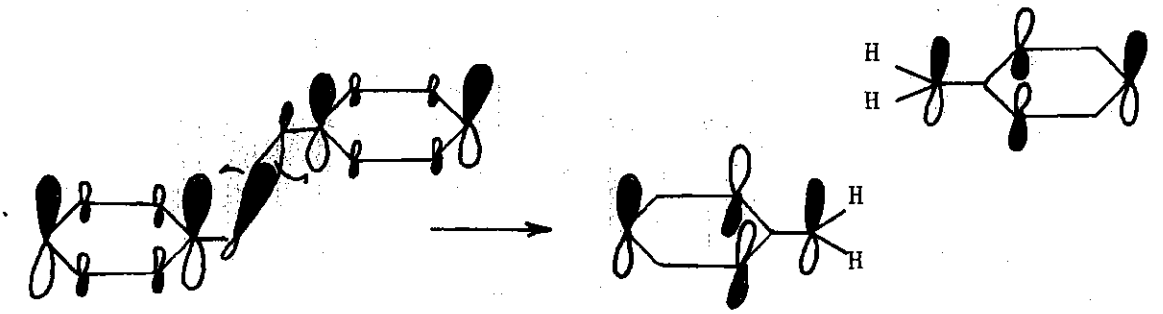


XXVI



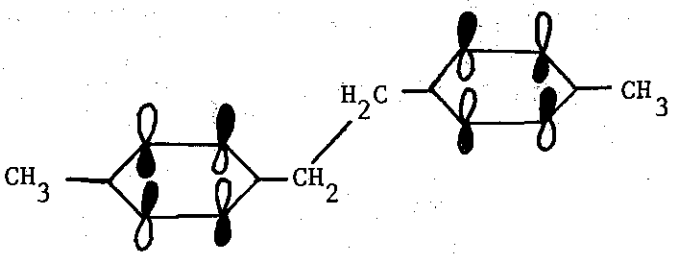
XXVII

orbitals of the dimethylene linkage with resultant in bond cleavage through electron repulsion. The net result of this cleavage would be to move an electron from an antibonding orbital of the radical anion to a non-bonding orbital of a benzyl anion (XXVIII).



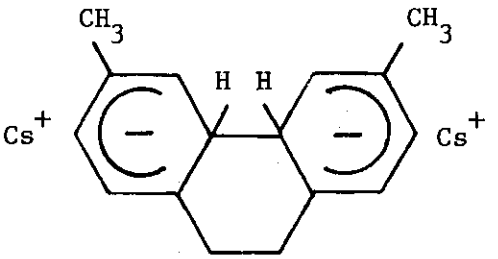
XXVII XXVIII

In reaction IV-125, carbonation of the products from the reaction of 1,2-di-p-tolylethane with Cs-K-Na alloy in THF at -75°C to 12°C for five hours gave mainly non-cleavage products and only a 6.2 mole % yield of p-tolylacetic acid. The resistance of 1,2-di-p-tolylethane to cleavage cannot be ascribed to failure to form the diradical anion, since ^{1}H NMR analysis indicates that the ratio of aromatic rings and reduced rings to carboxylic acid functions is 1:1. However the p-methyls would considerably destabilize the p,p'-dimethyl derivative of HOMO XXVII, since they would be on carbons of highest spin density. Thus, the most stable



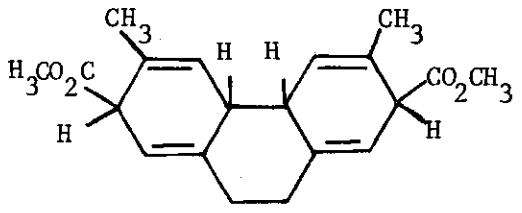
XXIX

diradical anion of 1,2-di-p-tolylethane would be HOMO XXIX. Since the electron spin density in the HOMO OF XXIX cannot overlap the sigma orbital of the dimethylene linkage, the molecule cannot readily cleave to give two benzyl anions. Therefore the diradical anion of 1,2-di-p-tolylethane would be expected to give reduction products similar to those of diphenylmethane and 1,3-diphenylpropane or could give the intramolecular cyclization product XXX through a process similar to that of the dimerization of toluene radical anion. The mass spectrum of the

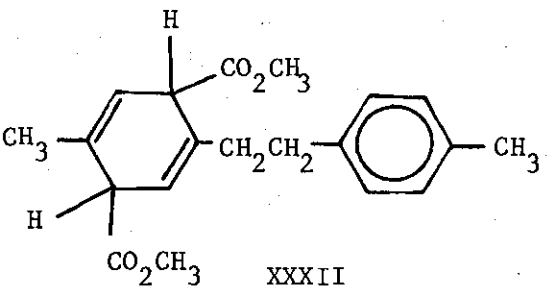


XXX

methyl esters of the acidic products from this reaction has a molecular ion at m/e 328, which is consistent with the methyl ester XXXI or XXXII.



XXXI



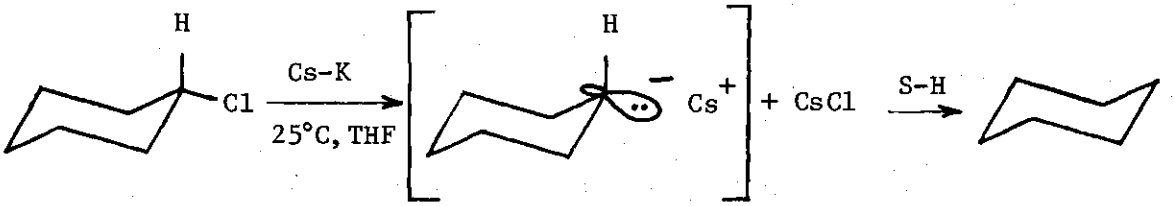
XXXII

Reaction of Cyclohexyl Chloride with Cs-K Alloy and 2,2,3-Triphenylpropyl Chloride with Cs-K-Na Alloy

The reaction of cyclohexyl chloride with Cs-K alloy was studied to determine to what extent cesium would be preferentially extracted from the alloy. As shown in Table 14, the data in reaction IV-33 suggests that cesium is extracted in a 10.2:1.0 ratio of cesium to potassium. The data for reaction III-127 indicates that this ratio may be as high as 21.4:1.0. Thus in systems such as alkyl chlorides or as hydrocarbons with high electron affinity (i.e., biphenyl) which can react with either cesium or potassium, the reaction with cesium is favored by a factor of at least ten.

The reaction of cyclohexyl chloride with Cs-K alloy is shown in Scheme 14. It is to be noted that the secondary carbanion once formed must be rapidly protonated by the solvent, since attempts to trap the carbanion by carbonation resulted in only a 1% yield of cyclohexyl-carboxylic acid.

Scheme 14



The reaction of 2,2,3-triphenylpropyl chloride with Cs-K-Na alloy was carried out to determine the reacting alkali metal by analysis of the

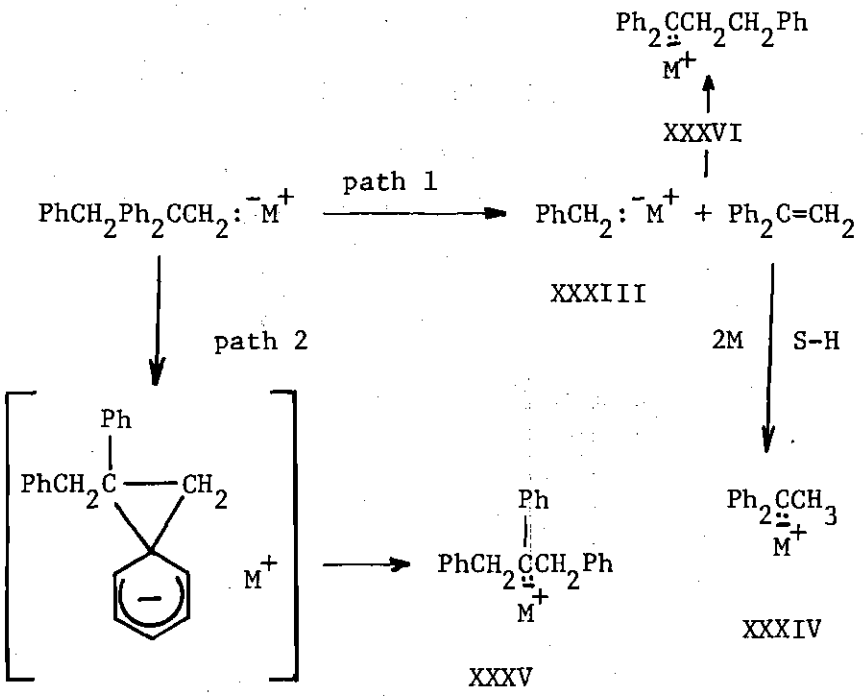
Table 14. Analysis of the Cesium Alloys for the Reacting Alkali Metal in the Reaction of Cyclohexyl Chloride and 2,2,3-Triphenylpropyl Chloride

Reaction	Alloy composition in Atom %		
	Initial	Final	Calculated*
cyclohexyl chloride	63.6% Cs	29.9% Cs	31.3% Cs
(III-127)	36.4% K	70.1% K	68.7% K
25° to 37°C			
cyclohexyl chloride	74.5% Cs	55.0% Cs	55.0% Cs
(IV-33)	25.5% K	45.0% K	45.0% K
25°C			
2,2,3-triphenylpropyl chloride	47.0% Cs	42.9% Cs	42.6% Cs
(IV-105)	34.1% K	37.3% K	36.6% K
-40°C	18.9% Na	19.8% Na	20.8% Na

*The calculated alloy composition is based on a 10.2:1.0 ratio of cesium to potassium in the reaction: $RCl + 2M \rightarrow R + M + MCl$.

alloy and to confirm that result by examining the products of the reaction, since the reaction of sodium, potassium, or cesium t-butoxide with 2,2,3-triphenylpropyllithium give different product distributions.[77] Since carbonation of the products of the reaction of 2,2,3-triphenylpropyl chloride with excess Cs-K-Na alloy at -45°C gave the acids of only the products of cleavage XXXIII and XXXIV and phenyl migration XXXV, the reacting cation is primarily cesium. No benzyl migration product,

Scheme 15



which is favored with potassium cation, was formed in this reaction. The following volatile acids were observed: phenylacetic acid (59.9% from XXXIII), 2,2-diphenylpropionic acid 12.6% from XXXIV), and 2-benzyl-2,3-diphenylpropionic acid (11.1% from XXXV). Because the weights of the

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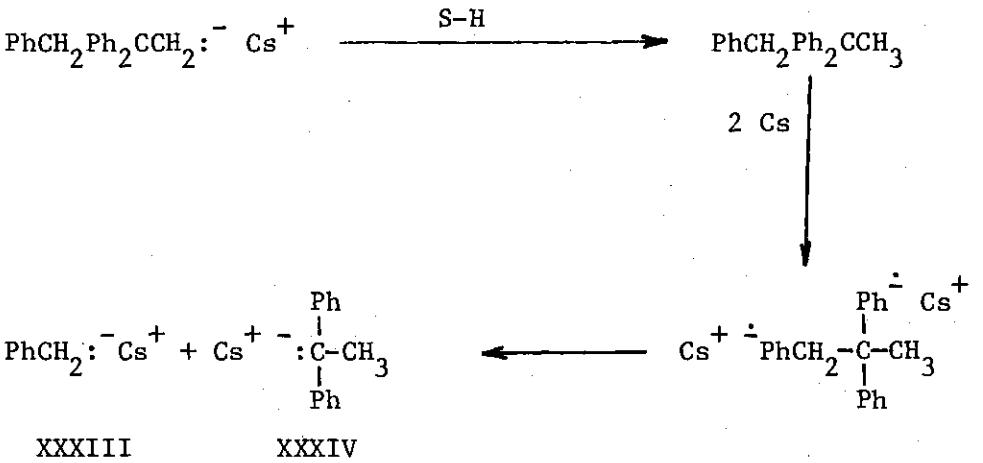
[77] E. Grovenstein, Jr. and R. E. Williamson, J. Amer. Chem. Soc., 97, 646 (1975).

neutral and acid products isolated from this reaction exceed that for the products isolated from this reaction exceed that for the volatile products most of the 1,1-diphenylethylene produced in path one must have polymerized. This is supported by the fact that the yield of phenylacetic acid is five times that of the 2,2-diphenylpropionic acid. Analysis of the acidic products by ^{1}H NMR indicates that the nonvolatile products from this reaction have a ratio of 52 aromatic protons to one acidic proton (CO_2H). This crudely indicates a polymeric dicarboxylic acid averaging ten monomer units in length with an average molecular weight of 1890.

It is possible that anion XXXIV is not produced by the metallation of diphenylethylene. An alternate route to anion XXXIV would be the protonation of 2,2,3-triphenylpropylcesium producing 2,2,3-triphenylpropane which in the presence of excess Cs-K-Na alloy cleaves to give XXXIII and XXXIV.

Scheme 16



Summary of Results

It has been demonstrated conclusively that it is the cesium metal in Cs-K-Na or Cs-K alloy which primarily reacts with either aromatic

hydrocarbons or alkyl chlorides to produce organoalkali species.

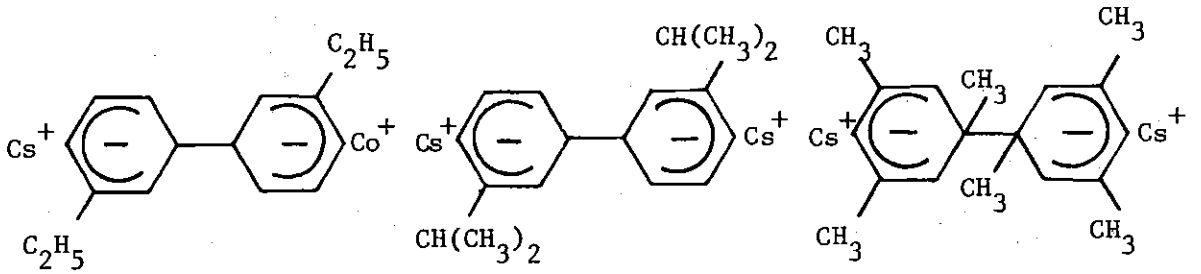
The primary reaction of Cs-K-Na alloy with aromatic hydrocarbons is formation of radical anions. These radical anions depending on their structure and the reaction temperature may dimerize, undergo intramolecular cyclization, cleave a carbon-hydrogen bond to form a carbanion, or cleave a carbon-carbon bond to give a pair of carbanions. Thus with benzene, toluene, and m-xylene at -45°C, the cesium benzenide, cesium toluenide, and cesium m-xylenide respectively are formed in good yield while p-xylene and t-butylbenzene do not react. At -45°C, these radical anions readily dimerize to give the dicesium 1,1'-dihydrobiphenylide, dicesium 3,3'-dimethyl-1,1'-dihydrobiphenylide, and dicesium 3,3',5,5'-tetramethyl-1,1'-dihydrobiphenylide respectively in high yield. The addition of 18-crown-6 to cesium benzenide or cesium m-xylenide results in protonation of the radical anion to give a radical which is reduced to the appropriate cyclohexadienyl anion. With 1,2-diphenylethane (bibenzyl), 2,3-dimethyl-2,3-diphenylbutane, and 1,2,2-triphenylpropane reaction with Cs-K-Na alloy evidently gives dicesium 1,2-diphenylethanide, dicesium 2,3-dimethyl-2,3-diphenylbutanide, and dicesium 1,2,2-triphenylpropanide respectively. Once formed at -75°C, these organocesium compounds immediately cleave to give benzylcesium, α,α-dimethylbenzylcesium, and a mixture of benzylcesium and α,α-diphenylethylcesium respectively. The Cs-K-Na alloy reacts with 1,3-diphenylpropane and 1,2-di-p-tolylethane at -75°C to give the dicesium 1,3-diphenylpropanide and the dicesium 1,2-di-p-tolylethanide. It is notable that in these reactions it is cesium not sodium or potassium which is the metal that primarily

reacts. The ability of cesium to form radical anions with benzene, alkylbenzenes, and polyphenylalkanes in near quantitative yield is due to the vastly superior reducing power of cesium over the other alkali metals in THF. Since cesium benzenide should be an intimate ion pair with a cation and anion of nearly equal size, this species readily forms insoluble ionic aggregates. Apparently these aggregates undergo a transition with increased temperature at -45°C to allow the closely packed radical anions to dimerize. The strong electrostatic interactions these aggregates between the large polarizable cesium cation and the dimeric dianions evidently provide considerable stabilization to help overcome the loss of aromaticity in the dimerization of the radical anions.

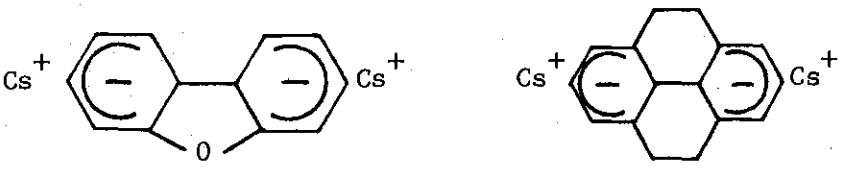
CHAPTER VI

RECOMMENDATIONS

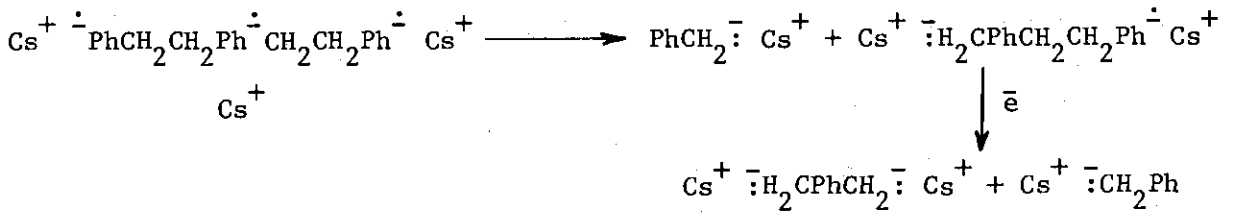
It would be interesting to extend the study of the reaction of Cs-K-Na alloy to include a number of compounds similar to those investigated in this work. For example, ethylbenzene, cumene, and mesitylene could react with Cs-K-Na alloy at -45°C in THF to give the corresponding cesium arenide which should dimerize to give dianions of the following respective structures:



Diphenylether and [2.2]metacyclophane could react with Cs-K-Na alloy at -75°C in THF to give a diradical anion which could undergo intramolecular coupling to give the following dianions respectively:



It would be interesting to react 1,4-bis(2-phenylethyl)benzene with Cs-K-Na alloy at -75°C in THF to form a tiradical anion which could cleave two carbon-carbon bonds in a concerted or the following stepwise manner:


Cs+ PhCH2CH2Ph CH2CH2Ph Cs+
Cs+
PhCH2: Cs+ + Cs+ :H2CPhCH2CH2Ph Cs+
ē
Cs+ :H2CPhCH2: Cs+ + Cs+ :CH2Ph

APPENDIX

CALCULATION OF THE COMPOSITION OF Cs-K-Na ALLOY FROM THE ANALYTICAL DATA OBTAINED IN REACTION III-153, THE REACTION OF BENZENE WITH Cs-K-Na ALLOY

This calculation as indicated in the instrumental and general procedures chapter is based on three experimentally determined parameters: the alloy weight, mmols of total base in an aqueous solution of the weighed alloy, and the weight of the cesium-potassium tetraphenylboron which can be precipitated from this solution. Thus, with three unknowns and three analytical measurements, three simultaneous equations where X = mg-atoms Na, Y = mg-atoms K, and Z = mg-atoms Cs can be written:

(1) $X + Y + Z = 5.384 \pm 0.01$ mmol MOH

(2) 22.9898 mg/mg-atom Na X + 39.102 mg/mg-atom K Y + 132.905 mg/mg-atom Cs Z = 415.3 ± 0.2 mg Cs-K-Na alloy

(3) 358.342 mg/mmol KTPB Y + 452.145 mg/mmol CsTPB Z = 1969 ± 2 mg Cs-KTPB

Solving equation (3) for Y in terms of Z:

(4) $Y = 5.495 \pm 0.006$ mmol $- 1.2618\ Z$

Substituting equation (4) into equation (1) and solving for X in terms of Z gives:

(5) $X = -0.111 \pm 0.016 + 0.2618\ Z$

Equation (2) can be solved for Z by substituting equation (4) for Y and equation (5) for X.

22.9898 mg/mg-atoms Na (- 0.111 ± 0.016 mmol + 0.2618 Z) +

39.102 mg/mg-atoms K (5.495 ± 0.006 mmol + 1.2618 Z) +

132.905 mg/mg-atoms Cs Z = 415.3 ± 0.2 mg Cs-K-Na alloy

89.585 Z = 203.0 ± 0.9

Z = 2.266 ± 0.009 mg-atoms Cs

Thus solving equations (4) and (5) for Y and X respectively:

Y = 2.636 ± 0.009 mg-atoms K

X = 0.482 ± 0.005 mg-atoms Na

Therefore the initial alloy composition in atom % can be determined by dividing the values of X, Y, and Z by equation (1).

% Cs = (100) 2.266 ± 0.009/5.384 ± 0.010 = 42.1 ± 0.3

% K = (100) 2.636 ± 0.009/5.384 ± 0.010 = 49.0 ± 0.3

% Na = (100) 0.482 ± 0.005/5.384 ± 0.010 = 8.9 ± 0.1

The final alloy composition, which was calculated in the same manner, was 33.9 ± 0.3 atom % Cs, 55.7 ± 0.4 atom % K, and 10.4 ± 0.1 atom % Na.

Since the initial alloy composition in mg-atoms was 40.14 mg-atoms Cs, 46.69 mg-atoms K, and 8.55 mg-atoms Na, the theoretical final alloy

composition can be calculated assuming an one to one reaction of cesium to benzene (13.41 mmols). Thus the theoretical final alloy would have a composition of 26.73 mg-atoms Cs, 46.69 mg-atoms K, and 8.55 mg-atoms Na, which in atom % is 32.6 atom % Cs, 57.0 atom % K, and 10.4 atom % Na.

However since the reaction products were accounted for in a 99.2 mole % yield (i.e., 1.20 mmol 1,4-dihydrobenzene, 1.96 mmol benzene, and 5.08 mmol 1,1',4,4'-tetrahydrobiphenyl), the final alloy composition can be estimated based on the extent of reduction or dimerization of the organic products. Hence for each molecule of 1,4-dihydrobenzene and 1,1',4,4'-tetrahydrobiphenyl two cesium atoms were consumed. Therefore 12.56 mg-atoms of cesium was extracted from the alloy giving a predicted alloy composition of 27.58 mg-atoms Cs, 46.69 mg-atoms K, and 8.55 mg-atoms Na, which in atom % is 33.3 atom % Cs, 56.4 atom % K, and 10.3 atom % Na. This predicted composition is very close to the experimental value of 33.9 atom % Cs, 55.7 atom % K, and 10.4 atom % Na, which indicates that very little over-reduction of the organic products occurred during hydrolysis of the organocesium adducts.

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VITA

Dean Earl Quest was born in Butler, Pennsylvania on April 6, 1949. At the age of three he moved to Erie, Pennsylvania where he attended public school. In June of 1967, he graduated with honors from Strong Vincent High School. In June of 1971, he graduated from the Pennsylvania State University with a B.S. degree in chemistry. In September of 1971, he began graduate studies in the School of Chemistry at the Georgia Institute of Technology. While at Georgia Tech, he became active in student government and served as the Graduate Student Body Vice-President in 1974-75. In October of 1977, he completed his requirements for the Doctor of Philosophy in Chemistry.

On August 28, 1971, he was married to the former Selena K. Davis of York, Pennsylvania. They have two children, Dene Jason and Joshua Earl.